

03500.015726.

PATENT APPLICATION

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

TAKEO TSUKAMOTO

Application No.: 09/941,595

Filed: August 30, 2001

For: ELECTRON-EMITTING DEVICE,
ELECTRON SOURCE AND
IMAGE-FORMING APPARATUS, AND
METHOD FOR MANUFACTURING
ELECTRON EMITTING DEVICE

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: Examiner: M. P. Hodges

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: Group Art Unit: 2879

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September 8, 2003

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

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TECHNOLOGY CENTER 280C

SECOND SUPPLEMENTAL INFORMATION DISCLOSURE STATEMENT

Sir:

In compliance with the duty of disclosure under 37 C.F.R. § 1.56 and in accordance with the practice under 37 C.F.R. §§ 1.97 and 1.98, the Examiner's attention is directed to the documents listed on the enclosed Form PTO-1449. Copies of the listed documents are also enclosed.

For a concise explanation of relevance for various non-English documents listed on the enclosed Form PTO-1449, the Examiner is directed to the corresponding English-language abstracts, English translations, and/or English counterparts, where available, as

indicated in association with the relevant non-English documents on the Form PTO-1449.

For the concise statement of relevance of non-English document CN 1181607A, the Examiner also is respectfully referred to English-language counterparts EP 0 836 217 A1 and WO 99/58748.

The Examiner's attention is also directed to the following U.S. Application:

| <u>APPLICATION NO.</u> | <u>FILING DATE</u> | <u>GROUP ART UNIT</u> |
|------------------------|--------------------|-----------------------|
| 09/506,289 | 2/18/00 | 2818 |
| 09/666,605 | 09/20/00 | 2811 |
| 09/955,137 | 9/19/01 | 2879 |
| 10/106,484 | 3/27/02 | 2879 |
| 10/234,213 | 9/5/02 | 2879 |
| 10/235,809 | 9/6/02 | 2878 |

A copy of each cited application is enclosed.

It is respectfully requested that the above information be considered by the Examiner and that a copy of the enclosed Form PTO-1449 be returned indicating that such information has been considered.

A check for \$180.00 in payment of the required fee is enclosed. Please charge any deficiency in this payment, or credit any overpayment, to Deposit Account 06-1205.

Applicant's undersigned attorney may be reached in our New York office by telephone at (212) 218-2100. All correspondence should continue to be directed to our address given below.

Respectfully submitted,



Attorney for Applicant

Registration No. 42,476

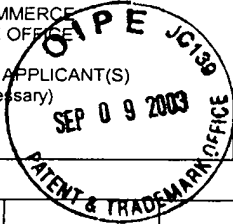
FITZPATRICK, CELLA, HARPER & SCINTO
30 Rockefeller Plaza
New York, New York 10112-3801
Facsimile: (212) 218-2200

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| FORM PTO 1449 (modified) | | | ATTY DOCKET NO. 03500.015726. | | APPLICATION NO. 09/941,595 | |
|---|------------------------|-----------------|---|------------|--------------------------------------|-------------------------------|
| U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE | | | APPLICANT Takeo Tsukamoto | | | |
| LIST OF REFERENCES CITED BY APPLICANT(S) (Use several sheets if necessary) | | | FILING DATE 08/30/01 | | GROUP 2879 | |
| Date Submitted to PTO: [DATE] | | | U.S. PATENT DOCUMENTS | | | |
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09/941,595

Takeo Tsukamoto

08/30/01

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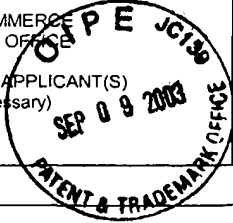
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| | DOCUMENT NUMBER | DATE | COUNTRY | CLASS | SUBCLASS | TRANSLATION YES/NO/ OR ABSTRACT |
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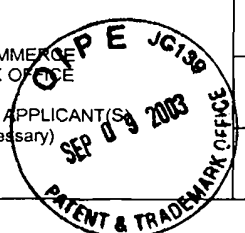


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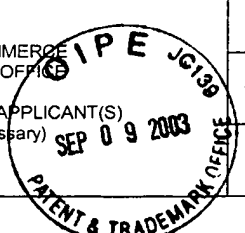


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| EXAMINER | | DATE CONSIDERED | |

*EXAMINER: Initial if reference considered, whether or not citation is in conformance with MPEP 609; Draw line through citation if not in conformance and not considered. Include copy of this form with next communication to applicant.

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ELECTRON-EMITTING DEVICE, ELECTRON SOURCE
AND IMAGE-FORMING APPARATUS, AND MANUFACTURING
METHODS THEREOF

5 BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an electron-emitting device, an electron source which uses a plurality of the electron-emitting devices, an image-forming apparatus such as a display apparatus, an exposure apparatus or the like which use the electron-emitting device and the electron source, and manufacturing methods thereof.

Related Background Art

15 There are conventionally known electron-emitting devices which are classified roughly into two kinds of electron-emitting devices: thermionic cathode and a cold cathode. The cold cathode is classified into a field emission type (hereinafter referred to as FE type), a metal/insulating layer/metal type (hereinafter referred to as MIM type) and a surface conduction type. Known as the FE type electron-emitting devices are electron-emitting devices which are disclosed by W. P. Dyke & W. W. Dolan, "Field emission," Advance in
20 Electron Physics, 8, 89 (1956), C. A. Spindt, "PHYSICAL Properties of thin-film field emission cathodes with molybdenum cones," J. Appl. Phys., 47, 5248 (1976) or
25

the like.

Known as examples of the MIM type electron-emitting device are electron-emitting devices disclosed by C. A. Mead, "Operation of Tunnel-Emission Devices,"
5 J. Apply. Phys., 32, 646 (1961) and so on.

Known as examples of the surface conduction type electron-emitting devices are electron-emitting devices disclosed by M. I. Elinson, Recio. Eng. Electron Phys.,
10 10, 1290 (1965) and so on.

10 The surface conduction type electron-emitting devices utilize a phenomenon where electrons are emitted by supplying a current to a thin small area film formed on a substrate in parallel with a surface of the film. Reported as the surface conduction type
15 electron-emitting devices are devices disclosed by Elinson, et al. described above which uses thin films of SnO_2 , devices which use thin films of Au [G. Dittmer: "Thin Solid Films," 9, 317 (1972)], devices which use thin films of $\text{In}_2\text{O}_3/\text{SnO}_2$ [M. Hartwell and C.G. Fonstad:
20 "IEEE Trans. ED Conf. "519 (1975)], devices which use thin films of carbon [Hisashi Araki, et. al.: shinku (Vacuum), Vol. 26, No. 1, p.22 (1983)] or the like.

Fig. 11 schematically shows a configuration of the device disclosed by M. Hartwell described above as a
25 typical example of the surface conduction type electron-emitting device. In Fig. 11, reference numeral 111 denotes a substrate. Reference numeral 114

designates an electrically conductive film which is composed of a thin film of a metal oxide formed by sputtering as an H-shaped pattern and an electron emitting region 115 is formed by an current supply treatment. In Fig. 11, a spacing L of 0.5 to 1 mm is reserved between element electrodes and W' is set at 0.1 mm.

It is conventionally general before emitting electrons to form the electron emitting region 115 on the surface conduction type electron-emitting device by subjecting the electrically conductive film 114 to a energization treatment called "forming". Speaking concretely, a DC voltage or pulse voltage is applied across both ends of the electrically conductive film 114 to locally break, deform or degenerate the electrically conductive film 114, thereby forming the electron emitting region 115 which is in an electrical condition of high resistance. At this stage, the electrically conductive film 114 is partially cracked and forms a gap.

The surface conductive electron-emitting device which has the gap formed as described above emits electrons from the electron emitting region 115 (vicinities of the gap) when a current is supplied to the device by applying a voltage to the electrically conductive film 114.

It is possible to compose an image-forming

apparatus by forming a plurality of electron-emitting devices such as that described above on an electron source substrate and combining it with an image-forming member composed of a fluorescent material or the like.

5 However, the electron-emitting device disclosed by M. Hartwell described above is not always satisfactory in its stable electron-emitting characteristic and electron-emitting efficiency, whereby it is extremely difficult under to provide an image-forming apparatus
10 which has high luminance and excellent operating stability.

 Accordingly, a treatment called activation treatment may be carried out as disclosed by Japanese Patent Application Laid-Open Nos. 08-264112, 08-162015,
15 09-027268, 09-027272, 10-003848, 10-003847, 10-003853 and 10-003854. The activation treatment step is a step of remarkably changing a device current I_f and an emission current I_e .

 Like the forming treatment, the activation step
20 can be carried out by repeating application of a pulse voltage to device in an atmosphere containing an organic substance. This treatment allows a film comprising of carbon and/or carbon compounds is deposited from the organic substance existing in the
25 atmosphere onto at least the electron emitting region to remarkably change the device current I_f and the emission current I_e , thereby making it possible to

obtain a more favorable electron emitting characteristic.

An example of conventional manufacturing method of the electron-emitting device will be described with reference to Figs. 19A through 19D.

First, a first electrode 2 and a second electrode 3 are disposed on a substrate 1 (Fig. 19A).

Then, an electrically conductive film 4 is disposed to connect the first and second electrodes. (Fig. 19B)

Then, the forming treatment described above is carried out. Speaking concretely, a second gap 6 is formed in a portion of the electrically conductive film 4 by flowing a current through the electrically conductive film (Fig. 19C).

Furthermore, the activation treatment described above is carried out. Speaking concretely, by supplying a voltage to the electrically conductive film, a carbon film 10 is formed on the substrate 1 within the second gap 6 and the electrically conductive film 4 in the vicinity of the gap 6. This activation treatment forms a first gap 7 which is narrower than the second gap, thereby forming an electron emitting region 5 (Fig. 19D).

25

SUMMARY OF THE INVENTION

A manufacturing method of the electron-emitting device according to the present invention comprises: a

step of disposing an electrically conductive member having a second gap on a substrate; a step of irradiating at least the second gap with an electron beam in an atmosphere comprising carbon compounds from
5 electron emitting means disposed apart from the electrically conductive member; and a step of applying a voltage to the electrically conductive member in an atmosphere containing a carbon compounds.

Furthermore, the manufacturing method of the
10 electron-emitting device according to the present invention comprises: a step of disposing a first and second electrically conductive members on a substrate with a second gap interposed; a step of irradiating at least the second gap with an electron beam in an
15 atmosphere comprising carbon compounds from electron emitting means disposed apart from the electrically conductive members; and a step of applying a voltage to the first and second electrically conductive members.

Furthermore, the manufacturing method of the
20 electron-emitting device according to the present invention comprises: a step of disposing an electrically conductive member having a second gap on a substrate; and a step of applying a voltage to the electrically conductive member while irradiating at
25 least the second gap with electron beam in an atmosphere comprising carbon compounds from electron emitting means disposed apart from the electrically

conductive member.

Furthermore, the manufacturing method of the electron-emitting device according to the present invention comprises: a step of disposing a first and
5 second electrically conductive members on a substrate with a second gap interposed; and a step of applying a voltage to the first and second electrically conductive members while irradiating at least the second gap with an electron beam in an atmosphere comprising carbon
10 compounds from electron emitting means disposed apart from the electrically conductive members.

Furthermore, the manufacturing method of the electron-emitting device according to the present invention comprises: a step of disposing an
15 electrically conductive member with a second gap on a substrate; and a step of irradiating at least the second gap with an electron beam in an atmosphere comprising a carbon compound from electron emitting means disposed apart from the electrically conductive
20 member during a period where a voltage is applied to the electrically conductive member.

Furthermore, the manufacturing method of the electron-emitting device according to the present invention comprises: a step of disposing a first and
25 second electrically conductive members with a second gap interposed on a substrate, and a step of irradiating at least the second gap with an electron

beam in an atmosphere comprising the carbon compound
from the electron emitting means disposed apart from
the electrically conductive members during a period
where a voltage is applied to the first and second
5 electrically conductive members.

Moreover, the manufacturing method according to
the present invention described above is applicable
preferably to a manufacturing method of an electron
source which has a plurality of electron-emitting
10 devices.

In addition, the manufacturing method according to
the described above present invention is applicable
preferably to a manufacturing method of an image-
forming apparatus which has an electron source and an
15 image-forming member.

The electron-emitting device according to the
present invention is characterized in that it is an
electron-emitting device which has a carbon film having
specific resistance of 0.001 Ωm or lower.

20 Furthermore, the electron-emitting device
according to the present invention described above is
applicable preferably to an electron source which has a
plurality of electron-emitting devices.

Moreover, the electron-emitting device according
25 to the present invention described above is applicable
preferably to an image-forming apparatus which has an
electron source and an image-forming member.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A and 1B are schematic diagrams showing a configuration of preferable embodiment of the electron-emitting device according to the present invention;

5 Figs. 2A, 2B, 2C and 2D are schematic diagrams showing manufacturing steps of the electron-emitting device shown in Figs. 1A and 1B;

Fig. 3 is a diagram showing a voltage waveform used to form an electron emitting region of the
10 electron-emitting device according to the present invention;

Fig. 4 is a schematic diagram showing electron irradiating means which is used at an activation step of the manufacturing method of the electron-emitting
15 device according to the present invention;

Fig. 5 is a schematic diagram showing an evaluating apparatus used to evaluate an electron emitting characteristic of the electron-emitting device according to the present invention;

20 Fig. 6 is a diagram showing relationship among an emission current I_e , a device current I_f and a device voltage V_f in the electron-emitting device according to the present invention;

Figs. 7A and 7B are diagrams showing a
25 configuration of a preferable embodiment for the electron source according to the present invention;

Figs. 8A and 8B are diagrams showing a voltage

waveform for the activation step of the electron source shown in Figs. 7A and 7B;

Figs. 9A and 9B are schematic diagrams showing a locus of an electron beam at the activation step of the electron source shown in Figs. 7A and 7B;

Figs. 10A and 10B are diagrams showing an another example of voltage waveform used at the activation step of the electron source according to the present invention;

Fig. 11 is a schematic diagram showing a conventional electron-emitting device;

Fig. 12 is a schematic configurational diagram showing an electron source having a simple matrix arrangement preferred as an embodiment of the electron source according to the present invention;

Fig. 13 is a schematic configurational diagram showing a display panel used in an embodiment of the image-forming apparatus according to the present invention which uses an electron source having the simple matrix arrangement;

Figs. 14A and 14B are diagrams showing fluorescent films on the display panel shown in Fig. 13;

Fig. 15 is a diagram exemplifying a driving circuit for driving the display panel shown in Fig. 13;

Fig. 16 is a schematic diagram showing an electron source having a ladder arrangement preferred as an embodiment of the electron source according to the

present invention;

Fig. 17 is a schematic diagram showing a display panel used in an embodiment of the image-forming apparatus according to the present invention which uses
5 the electron source having the ladder arrangement;

Fig. 18 is a block diagram showing an example of the image-forming apparatus according to the present invention;

Figs. 19A, 19B, 19C and 19D are schematic diagrams
10 showing an example of the manufacturing method of the electron-emitting device according to the present invention;

Fig. 20 is a schematic diagram showing a problem to be solved by the present invention;

15 Figs. 21A and 21B are schematic diagrams showing an example of the electron-emitting device according to the present invention;

Figs. 22A and 22B are schematic diagrams showing an example of the manufacturing method of the electron-emitting device according to the present invention;
20

Fig. 23 is a schematic diagram showing an example of the manufacturing method of the electron-emitting device according to the present invention;

Figs. 24A, 24B and 24C are schematic diagrams
25 showing an example of the manufacturing method according to the present invention;

Figs. 25D and 25E are schematic diagrams showing

an example of the manufacturing method according to the present invention; and

Figs. 26D, 26E and 26F are schematic diagrams showing an example of the manufacturing method
5 according to the present invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In order that an image-forming apparatus which uses electron-emitting devices displays a bright image
10 stably, it is desired to maintain an electron emission characteristic at a higher electron emitting efficiency, more stably and for a longer time.

The electron emitting efficiency means herein a ratio of a current emitted to vacuum (hereinafter
15 referred to as emission current I_e) relative to a current supplied between device electrodes (hereinafter referred to as device current I_f) when a voltage across a pair of device electrodes of an electron-emitting device which are opposed to each other is applied.

20 When a high electron emission efficiency can be controlled stably for a long time, it is possible to obtain an image-forming apparatus, for example a flat display which uses a fluorescent material, for example, as an image forming member and forms a bright high
25 quality image with low electric power.

For such application, it is demanded that the emission current I_e is sufficient at a practical

voltage level (for example, 10 V to 20 V), that the emission current I_e and the device current I_f are not varied remarkably during driving, and that the emission current I_e and the device current I_f are not lowered
5 for a long time.

However, as described above, the conventional manufacturing method of the surface conduction type electron-emitting device poses problems which are explained below.

10 Characteristics of the device such as an electron emission efficiency and a life of the device are dependent on a structure and stability of a carbon film 10 (see Fig. 19D) comprising of carbon and/or carbon compounds which is deposited at the activation step.

15 Furthermore, a shape of the second gap 6 which is formed at the forming step described above may have a shape which is ununiform in its width as schematically shown in Fig. 20. Fig. 20 is a schematic plan view of a device which has been subjected to the forming step
20 (Fig. 19C). Furthermore, the second gap 6 which is formed at the forming step may remarkably meander between the electrodes 2 and 3. When the second gap 6 formed at the forming step has an ununiform shape as described above, an ununiform electric field is formed
25 in the gap 6 described above by applying a voltage across the device electrodes 2 and 3.

Even when the second gap 6 has the ununiform

shape, it can be covered to substantially narrow its width at the activation step by depositing the carbon film 10 comprising of the carbon and/or the carbon compound on the substrate 1 in the gap 6 and the electrically conductive film 4 in the vicinity of the gap 6.

As a result, by the activation step, variations of the width of the gap 6 formed at the forming step can be reduced, and the emission current I_e and the device current I_f can be enhanced.

However, ununiformities of distances from the device electrodes 2 and 3 to the gap 6 (meandering of the gap 6) cannot be basically reduced even by carrying out the activation step described above.

Furthermore, a deposited amount of the carbon film 10 which is formed at the activation step may be ununiform dependently on an ununiformity in the width of the gap 6 formed at the forming step.

Due to these ununiformities, an effective voltage applied to the first gap 7 is ununiform when the voltage is applied to the device electrodes 2 and 3. Furthermore, the emission current I_e may be different from location to location or a high electric field is applied locally, thereby producing a region which is easily deteriorated.

Furthermore, the conventional manufacturing method may not provide a required electron emission efficiency

makes the emission current I_e variable among devices, and allows the characteristics to be varied or degraded during the driving.

In order to obtain a high-definition image-forming apparatus which is applicable to a flat display using electron-emitting devices, it is therefore necessary to form the electron emitting region of an electron-emitting device, a carbon film comprising of carbon and/or a carbon compound which has a more preferable structure and a more preferable stability.

It is therefore necessary to deposit carbon and/or a carbon compound having preferable structure and stability on the electron emitting region of the electron-emitting device in order to obtain the high-definition image-forming apparatus which is applicable to the flat television or the like using the electron-emitting devices.

In view of the problems described above, the present invention achieves a manufacturing method of an electron-emitting device which exhibits favorable electron emission efficiencies uniformly and stably for a long time, composes manufacturing methods of an electron source and an image-forming apparatus using the manufacturing of the electron-emitting device, and provides an electron-emitting device and an electron source which can exhibit favorable electron emission efficiencies uniformly by the manufacturing method, and

provides an image-forming apparatus which uses the electron source and is excellent in a high luminance uniform display characteristic. In view of the problems described above, the present invention

5 achieves a manufacturing method of an electron-emitting device which exhibits favorable electron emission efficiencies for a long time, composes manufacturing methods of an electron source and an image-forming apparatus using the manufacturing of the electron-

10 emitting device, and provides an electron-emitting device and an electron source which have favorable uniform electron emission efficiencies, and a high luminance image-forming apparatus which uses the electron source and is excellent in a display

15 characteristic.

Now, an embodiment of the manufacturing method according to the present invention will be described in detail with reference to Figs. 1A and 1B, 2A to 2D and 4.

20 Figs. 1A and 1B are schematic diagrams showing a configuration of a surface conduction type electron-emitting device to which the present invention is preferably applied: Fig. 1A being a plan view and Fig. 1B being a sectional view taken along a 1B-1B line in Fig. 1A. Figs. 2A through 2D and 4 are schematic

25 diagrams showing a portion of the manufacturing method according to the present invention.

In Figs. 1A and 1B, 2A to 2D and 4, reference numeral 11 denotes a substrate, reference numerals 12 and 13 designate device electrodes, reference numeral 14 denotes an electrically conductive film, reference numeral 15 denotes a carbon film (electrically conductive film) having a main component of carbon, reference numeral 100 denotes an electron emitting region, reference numeral 16 designates a second gap and reference numeral 17 denotes a first gap.

10 (Step A)

First, the electrodes 12 and 13 which are opposed to each other are to be formed. For this purpose, the substrate 11 is washed sufficiently using a detergent, pure water, an organic solvent and the like, and the electrodes 12 and 13 are formed on the substrate 11 using a photolithography technique after depositing an electrode material by a vacuum deposition method, sputtering process or the like (Fig. 2A). Alternately, the electrodes can be formed by a printing method such as offset printing method. It is preferable to use the printing method, the offset printing method in particular, since it permits inexpensively forming the electrodes so as to have large areas.

Usable as the substrate 11 in the present invention is a glass substrate which is composed of glass having reduced contents of impurities such as Na, silica glass, soda lime glass, soda lime glass coated

with SiO_2 by the sputtering process, a ceramic substrate or an Si substrate.

A general conductive material is usable as a material of the electrodes 12 and 13. For example, the material is selected adequately out of metals such as Ni, Cr, Au, Mo, W, Pt, Ti, Al, Cu and Pd or alloys thereof, metals and metal oxides such as Pd, Ag, Au, RuO_2 and Pd-Ag, printing conductive materials composed of any of the metals, alloys and metal oxides described above and glass or the like, transparent electrically conductive materials such as In_2O_3 - SnO_2 and semiconductor conductive materials such as polysilicon.

A spacing L between the device electrodes, length W of the device electrodes, a shape of the electrically conductive film 14 and the like are designed taking an application mode or the like into consideration. The spacing L between the device electrodes is preferably within a range from hundreds of nanometers to hundreds of micrometers, more preferably within a range from several micrometers to scores of micrometers taking into consideration a voltage or the like to be applied across the device electrodes.

Taking a resistance value of the electrodes and electron emission efficiencies into consideration, the length W of the device electrodes is preferably within a range from several micrometers to hundreds of micrometers and film thickness d of the device

electrodes 12 and 13 is preferably within a range from scores of nanometers to several micrometers.

The electron-emitting device can have the configuration shown in Figs. 1A and 1B but also a
5 configuration wherein the electrically conductive film 14 and the device electrodes 12 and 13 which are opposed to each other are laminated in this order on the substrate 11.

(Step B)

10 Then, the electrically conductive film 14 is to be formed. By applying an organometal solution, for example, an organic metal film is formed on the substrate 11 on which the electrodes 12 and 13 are disposed. The organometal solution is a solution of an
15 organometallic compound which has a main component of the metal selected as the material of the electrically conductive film 14 described above. The organometal film is baked and patterned by lifting off or etching, thereby forming the electrically conductive film 14
20 (Fig. 2B). Though the organic metal film is formed by applying the organometal solution in the above description, this application method is not limitative and the vacuum deposition method, the sputtering process, a chemical vapor deposition method, a
25 dispersion coating method, a dipping method, a spinner method, an ink-jet method or the like may be used to form the electrically conductive film 14.

An ink-jet method is preferable from a viewpoint of productivity since it permits imparting minute liquid drops of 10 nanograms to scores of nanograms to the substrate with high repeatability and makes it unnecessary to pattern the electrically conductive film by the photolithography or a vacuum process. To form the electrically conductive film by the ink-jet method, it is possible to use a bubble jet type apparatus which uses an electrothermal energy conversion element as an energy generating element or a piezo-jet type apparatus which uses a piezoelectric element. Used as calcining (baking) means for the liquid drops described above is electromagnetic wave irradiating means, heated air blowing means or means to heat the substrate as a whole. Usable as the electromagnetic wave irradiating means is, for example, an infrared lamp, argon ion laser or a semiconductor laser or the like.

A material for the electrically conductive film can be selected from among metals such as Pd, Pt, Ru, Ag, Au, Ti, In, Cu, Cr, Fe, Zn, Sn, Ta, W and Pd, oxides such as PdO, SnO₂, In₂O₃, PbO and Sb₂O₃, borides such as HfB₂, ZrB₂, LaB₆, CeB₆, YB₄ and GdB₄, carbides such as TiC, ZrC, HfC, Ta, C, SiC and WC, nitrides such as TiN, ZrN and HfN, and semiconductors such as Si or Ge.

Film thickness of the electrically conductive film is set adequately taking into consideration a step

coverage to the device electrodes 12 and 13, resistance value between the device electrodes 12 and 13, etc. and the thickness is preferably within a range from several angstroms to hundreds of nanometers, or more preferably within a range from 1 nm to 50 nm. A resistance value R_s of the electrically conductive film is preferably within a range from 1×10^2 to $1 \times 10^7 \Omega/\square$. For calculation of R_s , resistance R of a thin film which has a width w and a length l measured in a longitudinal direction is taken as $R = R_s (l/w)$.

(Step C)

Then, the forming step is carried out to form the second gap 16 in the electrically conductive film (electrically conductive member) 14. Speaking concretely, a voltage is applied to a pair of the electrodes 12 and 13 to flowing a current through the electrically conductive film 14, thereby forming the gap 16 which has a local structural variation such as breakage, deformation or degeneration in a portion of the electrically conductive film 14 (Fig. 2C). Though the electrically conductive film 14 is completely separated into right and left sections in Fig. 2C, these sections may be partially connected to each other. Therefore, the electrically conductive film 14 in which the gap 16 has been formed at the forming step described above may be a pair of electrically conductive films (electrically conductive members)

opposed to each other with the gap 16 interposed or the electrically conductive film (electrically conductive member) 14 which has the gap 16.

Fig. 3 shows an example of voltage waveform for an energization treatment described above. In Fig. 3, a pulse width T_1 is set freely within a range from 1 μ sec to 10 m sec and a pulse interval T_2 is set freely within a range from 10 μ sec to 10 msec. A pulse height is selected dependently on a material and thickness of the electrically conductive film. Under conditions which are described above, a pulse voltage is applied for several seconds to scores of minutes. When a current value during voltage application is preliminarily measured, a current value not exceeding a certain set value is usable to judge that formation of the gap 16 has been completed. For example, a resistance value is determined by measuring a current which is supplied by applying a voltage on the order of 0.1 V and when the resistance is larger than 1 M Ω , the formation is terminated by stopping the current. (Step D)

The activation step is carried out to form the carbon film 15 having the main component of carbon is formed on the electrically conductive film 14 in which the second gap 17 has been formed as described above (Fig. 2D). The device current I_f and the emission current I_e can be remarkably enhanced at this step.

According to the present invention, electron emitting means 41 is separately disposed outside the electron-emitting device as shown in Fig. 4 at the activation step and the carbon film 15 having the main component of carbon is formed by applying a voltage across the electrodes 12 and 13 while irradiating any one of areas (1) through (3) mentioned below in the vicinity of the gap 16 with an electron beam emitted from the electron emitting means. That is, voltage application to the electrodes 12 and 13 is carried out simultaneously with irradiation with the electron beam from the electron emitting means.

The area irradiated with the electron beam described above is:

- (1) The substrate 11 in the gap 16 described above
- (2) The substrate 11 in the gap 16 described above and the electrically conductive film 14 in the vicinity of the gap 16 or

- (3) The substrate 11 in the gap 16 described above, the electrically conductive film 14, and additionally the electrodes 12 and 13. It is preferable to irradiate the region (3) described above with the electron beam.

Furthermore, it is preferable at the activation step described above of carrying out the voltage application to the electrodes 12 and 13 by repeatedly applying a pulse voltage. Moreover, it is preferable

for the present invention to apply a bipolar pulse voltage as shown in Fig. 2D or Fig. 22B.

The carbon film 15 can be formed by repeatedly applying a pulse voltage across the electrically
5 conductive film 14 (the pair of electrodes 12 and 13) in an atmosphere containing a carbon compound gas (an organic substance gas) and irradiating the vicinity of the gap 16 with the electron beam emitted from the electron emitting means 41 disposed apart from the
10 electron-emitting device.

Fig. 4 schematically shows an apparatus used to irradiate the vicinity of the gap 16 with an external electron beam. In Fig. 4, reference numeral 41 denotes electron emitting means. The electron-emitting device
15 and the electron emitting means 41 are disposed in the same vacuum vessel. Usable as the electron emitting means 41 is a structure which uses a thermionic cathode as an electron beam source and accelerates an electron beam by applying an accelerating voltage.

20 It is not necessary to focus the electron beam emitted from the electron emitting means 41 only on the gap 16, but it is preferable to spread the electron beam to an extent not smaller than several micrometers around the gap 16 taking into consideration the voltage
25 applied across the electrodes (12, 13) and a partial pressure of the carbon compound gas at the activation step.

When too large a region is irradiated with the electron beam, however, the carbon compound may be deposited on an unnecessary area. It is therefore preferable to shield the electron beam emitted from the electron emitting means 41 with electron beam shielding means 42 to suppress spreading of the electron beam.

It is preferable to set the accelerating voltage described above set to 1 kV to 20 kV. In other words, it is preferable to irradiate the region with an electron beam which has an energy not lower than 1 keV and not higher than 20 keV. The electron beam may be emitted like a DC voltage or as pulses in synchronization with the pulse voltage applied across the electrodes 12 and 13 described above. It is preferable to apply the pulse voltage to the device electrodes described above while emitting the electron beam continuously (like the DC voltage).

At the activation step of the present invention, it is preferable to apply a voltage to the device electrodes 12 and 13 while irradiating with the electron beam emitted from the electron emitting means 41. In other words, any one of the regions (1) through (3) described above is irradiated with the electron beam emitted from the electron emitting means while the voltage is being applied to the device electrodes 12 and 13.

The carbon films 15 described above which are

formed at the activation step of the present invention is connected to the electrodes 12 and 13 described above respectively by way of the electrically conductive film 14 or directly.

5 Furthermore, the electrically conductive films (carbon films) 15 which are formed at the activation step described above are opposed to each other with the first gap 17 interposed as shown in Fig. 2D. Though the carbon films 15 are completely separated into right and left sections taking the first gap 17 as a border
10 in Fig. 2D, these films may be partially connected to each other. Accordingly, the carbon films 15 formed in the activation step may be a pair of carbon films (electrically conductive members) 15 opposed to each
15 other with the gap 17 interposed or a carbon film (electrically conductive member) 15 which has the gap 17.

 As the carbon compound (organic substance) to be contained in the atmosphere at the activation step
20 described above, there can be mentioned aliphatic hydrocarbons such as alkane, alkene and alkyne, aromatic hydrocarbons, alcohols, aldehydes, ketones, amines, and organic acids such as phenol, carboxylic acid and sulfonic acid: concretely, usable carbon
25 compounds are saturated hydrocarbons such as methane, ethane and propane which are expressed by C_nH_{2n+2} , unsaturated hydrocarbons such as ethylene and propylene

which are expressed by a constitutional formula of C_nH_{2n} , benzene, toluene, methanol, ethanol, formaldehyde, acetraddehyde, acetone, methyl ethyl ketone, methyalmine, ethylamine, phenol, formic acid, 5 acetic acid, propionic acid or mixtures thereof.

It is considered that at the conventional activation step described above, the carbon compound (organic substance) existing in the atmosphere is decomposed only by a current supplied through the 10 second gap 16, the carbon and/or carbon compound is deposited onto the substrate within the second gap 16 and the electrically conductive film 14 in the vicinity of the gap 16, and electrons emitted from the vicinity of the gap 16 (the gap 17 which is being formed) 15 irradiate the carbon or carbon compound and crystallize a portion of the carbon or carbon compound, thereby imparting electrical conductivity.

A crystalline structure of the carbon film 15 obtained in the activation step contains a graphite 20 structure and/or an amorphous structure. Furthermore, the carbon film 15 may have such an intermediate structure in the course of its formation. The carbon film 15 can have a high electrical conductivity when it has the graphite structure, but its electrical 25 conductivity is lowered when the film has the amorphous structure. A degree of crystallinity produces a strong influence on characteristics of the electron-emitting

device, an electron emission efficiency in particular which is described later.

The degree of crystallinity denotes a proceeding degree of a substance to change from an amorphous
5 condition via a condition where a periodic structure is disordered relatively remarkably to a complete crystal structure.

Furthermore, the conventional activation step tends to allow the carbon or carbon compound deposited
10 in the gap 16 to be deposited, in particular, into relatively narrow gaps in the gap 16 as the step proceeds. As a result, the carbon film 15 is formed in a "disordered" structure.

Accordingly, the conventional manufacturing method
15 produces "disordered" structure of the carbon film 15 as the activation step proceeds, whereby some locations of the deposited carbon or carbon compound are not irradiated sufficiently with the electrons emitted from the vicinity of the gap 16. In such a condition, a
20 film of the carbon or carbon compound deposited in the vicinity of the gap 16 grows in a condition where it contains a number of regions having low degrees of crystallinity, whereby the carbon film 15 thus obtained has a low electrical conductivity. It is considered
25 that the low electrical conductivity is a result caused by insufficient irradiation with the electron beam in the growing step of carbon film 15.

When the carbon film contains the number of regions having low degrees of crystallinity as described above, it is considered that a crystalline structure of the carbon film 15 is gradually changed by bombardment with the electrons emitted from the electron emitting region or due to heat generation caused by the device current I_f , thereby changing a degree of crystallinity from the amorphous structure to the graphite structure. Furthermore, it is considered that resistance of the carbon film 15 is changed simultaneously, thereby gradually changing an electrical conduction characteristic of the device.

Change of the electrical conduction characteristic results in variations of electron-emitting characteristics of devices, thereby allowing luminance to be variable in case of an image-forming apparatus for which a number of devices desirably have uniform characteristics.

In contrast, the manufacturing method of electron-emitting device according to the present invention which uses an electron beam from outside the device is capable of irradiating the carbon film being formed in the second gap 16 sufficiently with the electron beam. Accordingly, the manufacturing method according to the present invention is capable of accelerating a change of a physical property of the carbon film, thereby efficiently forming an electrically conductive film

composed mainly of a carbon film which has a sufficiently high degree of crystallinity and a high electrical conductivity. As a result, the manufacturing method according to the present invention is capable of restraining the deterioration of the physical property of the carbon film during the driving as described above. Accordingly, the manufacturing method according to the present invention stabilizes the electron emitting characteristic of the device.

The manufacturing method according to the present invention is capable of controlling specific resistance of the electrically conductive film (carbon film) having the main component of carbon to $0.001 \Omega\text{m}$ or lower.

Furthermore, the manufacturing method of an electron source according to the present invention permits using an electron beam emitted from an electron emitting region of an adjacent electron-emitting device as the electron beam to irradiate the electron emitting region. This technique makes it unnecessary to dispose separate electron emitting means for electron beam irradiation as shown in Fig. 4.

Though the carbon film may be formed partially thick and shadowed regions which can hardly be irradiated with electron may be produced when a reaction to form the carbon film is made ununiform by the "disordered" structure, the manufacturing method

according to the present invention makes it possible to irradiate the carbon film at different angles by disposing external electron emitting means as described above and receiving electrons from the other adjacent
5 device.

Description will be made below of a technique to use an electron beam emitted from a different electron-emitting device.

Description will be made taking an example wherein
10 two devices are disposed adjacent to each other so that the devices use a device electrode commonly.

When the two electron-emitting devices are adjacent to each other, it is possible to irradiate a vicinity of an electron emitting region of an electron-emitting device with an electron beam emitted from an
15 electron emitting region of the other electron-emitting device, thereby forming a carbon film (electrically conductive film) having a main component of carbon while irradiating the electron emitting region with the
20 electron beam. Since electrons are emitted from a side of a cathode toward a side of an anode at this time, electrons can be led to the electron emitting regions of the electron-emitting devices with a higher
25 efficiency by matching directions of electrons emitted from the two electron-emitting devices with each other. Owing to a structure wherein the one of the device electrodes is used commonly by the two

electron-emitting devices adjacent to each other or either device electrode of the electron-emitting device is electrically connected to either electrode of the other electron-emitting device in particular, the
5 embodiment allows each of the electron-emitting devices to irradiate the electron emitting region of the other electron-emitting device. In other words, it is possible to completely match electron emitting directions with each other and irradiate the vicinity
10 of an electron emitting region with an electron beam emitted from another electron emitting region by setting a device electrode commonly used or device electrodes connected to each other at a ground potential and applying AC voltages which are deviated
15 in phases from each other in phases, for example voltages deviated π in phases, to a pair of electrodes. As a result, it is possible to efficiently form electrically conductive films (carbon films) having a main component of carbon on two electron emitting
20 regions substantially at the same time.

Figs. 7A and 7B are schematic diagrams showing a configuration of an electron source used for the embodiment: Fig. 7A being a plan view and Fig. 7B being a sectional view. In Figs, 7A and 7B, reference
25 numeral 71 denotes a substrate on which a common device electrode 72, and device electrodes 73 and 74 are formed. An electrically conductive film 75, an

electron emitting region 79 and a carbon film 76 are formed between a pair of device electrodes (referred to as an electrode pair A) consisting of the common device electrode 72 and the device electrode 73 to compose an electron-emitting device A. Furthermore, an electrically conductive film 77, an electron emitting region 80 and a carbon film 78 are formed between a pair of electrodes (referred to as a device electrode pair B) consisting of the common device electrode 72 and the device electrode 74 to compose an electron-emitting device B.

It can be regarded that the electron source has a basic configuration wherein a device is composed by arranging two electron-emitting devices similar to that described with reference to Figs. 1A and 1B in series by way of the common device electrode 72.

The electrodes 72 through 74 and the electrically conductive films 75 and 77 of the electron-emitting devices described above are formed by a method which is similar to that to form the electron-emitting device described above. Furthermore, a spacing L1 between the electrodes, and a length W and a film thickness of the electrodes are determined taking electron emission efficiencies into consideration. In Figs. 7A and 7B, the two electrode pairs have the same spacing L1 and the three electrodes have the same length. Furthermore, a width L2 of the common device electrode

72 is set taking into consideration a distance at which the electron beam emitted from the electron emitting region can reach the adjacent electron emitting region. An overlapping width of the device electrode over the electrically conductive film is optional so far as electrical conduction establishes between these members.

The electron emitting regions 79 and 80 can be simultaneously formed by grounding the common device electrode 72, connecting the device electrode 73 to the device electrode 74 to set these electrodes at an equal potential and applying a voltage simultaneously to the electrode pairs A and B.

For the activation treatment of two electron-emitting devices which are adjacent to each other as shown in Figs. 7A and 7B, the device can be irradiated with an electron beam emitted from the other device. Concrete procedures for the irradiation will be described below.

The common device electrode 72 is grounded, and a pulse voltage source (not shown) is connected to the device electrodes 73 and 74.

Figs. 8A and 8B exemplify voltage waveforms a and b of rectangular pulses to be applied like AC voltages to the device electrode 73 and the device electrode 74 respectively. As seen from Figs. 8A and 8B, pulse voltage which are different π in phases are applied to

the electrodes respectively.

Now, electrons flow through the electron emitting region in a direction from an electrode at relatively low potential toward an electrode at a high potential and a part of the electrons are emitted in the same direction as an electron beam. When voltages such as those shown in Figs. 8A and 8B are applied, electron beams are therefore emitted alternately in a direction from the electron emitting region 79 toward the electron emitting region 80 and a direction from the electron emitting region 80 toward the electron emitting region 79.

Figs. 9A and 9B schematically show a manner of alternate emission of electron beams. Each time a polarity of a pulse voltage changes, a direction of an electron beam is changed as shown in Figs. 9A and 9B. In case of Fig. 9A, an electron beam emitted from the electron emitting region 79 irradiates a vicinity of the electron emitting region 80. In case of Fig. 9B, in contrast, an electron beam emitted from the electron emitting region 80 irradiates a vicinity of the electron emitting region 79.

Voltage waveforms such as those shown in Figs. 10A and 10B are usable as another pulse pattern. In this case, pulse voltages which are $\pi/2$ different in phases from each other are applied to the device electrodes 73 and 74 respectively. This waveform pattern prevents an

electron beam from being emitted from an electron
emitting region while an electron beam is emitted from
another electron emitting region and allows the
electron source to receive the electron beam in a
5 direction only, thereby preventing interference from
taking place between electron beams which are emitted
in two directions.

Furthermore, the present invention provides a
manufacturing method described below which is capable
10 of reducing characteristic variations between the
devices caused due to the meandering of the second gap
16 produced at the forming step described above.

In other words, another embodiment of the present
invention is configured to carry out the activation
15 step described above directly between a pair of device
electrodes (electrically conductive members) 12 and 13
having relatively excellent linearities without using
the electrically conductive film 14 described above.
Fig. 21A is a schematic plan view showing an electron-
20 emitting device in this embodiment and Fig. 21B is a
schematic sectional view of the electron-emitting
device. Figs. 22A, 22B and 23 are schematic diagrams
showing partial process of the manufacturing method
described above. Herein, in the schematic diagrams
25 shown in Figs. 21A and 21B, a first gap 17 is traced in
completely straight lines for easy understanding of the
present invention. Further, though a carbon film 15 is

completely separated taking the first gap 17 as a border in Figs. 21A and 21B, the carbon film 15 may be partially connected. Accordingly, the carbon film 15 which is formed at the activation step described above
5 may be a pair of carbon films 15 which are opposed to each other via the gap 17 or a carbon film 15 which has the gap 17.

The other manufacturing method described above according to the present invention is configured to
10 dispose a pair of device electrodes (electrically conductive members) 12 and 13 on a substrate 11 with a gap L interposed (Fig. 22A). In this embodiment, the gap between the device electrodes 12 and 13 corresponds to the first gap 16 described above.

15 Then, the activation step according to the present invention is carried out. At this activation step, electron emitting means is separately disposed and the carbon film 15 is formed by applying a voltage to the electrodes 12 and 13 while irradiating either of
20 regions (1) and (2) mentioned below with an electron beam emitted from the electron emitting means (Figs. 22B and 23). In other words, the voltage is applied to the electrodes 12 and 13 simultaneously with irradiation with the electron beam from the electron
25 emitting means.

The region to be irradiated with the electron beam described above is either:

(1) The substrate 11 between the device electrodes 12 and 13 described above or

(2) The substrate 11 between the device electrodes 12 and 13 described above and the electrodes (12 and 13).

The embodiment is therefore capable of forming the carbon film 15 on the device electrodes 12 and 13 and the insulating substrate 11 between the device electrodes as well as the first gap 17 between the device electrodes 12 and 13.

Fig. 23 is a schematic diagram showing an apparatus for irradiation with an external electron beam. The electron irradiating apparatus shown in Fig. 23 has a configuration which is basically the same as that of the apparatus shown in Fig. 4. In Fig. 23, reference numeral 51 denotes electron emitting means. Though the electron emitting means 51 may be disposed in a vacuum vessel for electron-emitting device, it is possible as occasion demands to dispose the electron emitting means in a vacuum vessel separate from a vacuum vessel accommodating the substrate 11 and evacuate the electron emitting means differentially.

When the electron emitting means is to be evacuated differentially, a pinhole for electron beam permeation (52 in Fig. 23) is formed so that an internal pressure of the vacuum vessel accommodating the substrate 11 can be separated from an internal

pressure of the vacuum vessel accommodating the electron emitting means 51 due to low conductance of the pinhole.

5 A structure which uses a thermionic cathode as an electron source and accelerates an electron beam by applying an accelerating voltage may be used as the electron emitting means 51. Furthermore, electron beam shielding means 53 may be disposed to delicately control the region irradiated with the electron beam.

10 The device electrodes 12 and 13 and/or the substrate 11 between the device electrodes may be irradiated with the electron beam like a DC voltage or a pulse voltage in synchronization with a pulse voltage applied to the electrodes.

15 Accordingly, the present invention makes it unnecessary to use the electrically conductive film 14 (see Figs. 1A and 1B) which is electrically connected to the device electrodes and the "forming" to form the second gap 16 in the electrically conductive film, 20 which are required in the activation step.

In other words, the present invention makes it possible to dispose the carbon film 15 and the first gap 17 in a spacing L (several micrometers to scores of micrometers) between the electrodes which is far 25 broader than the second gap 16, described above, by irradiation with the external electron beam.

Furthermore, the second gap 16 formed in the device

shown in Figs. 21A and 21B corresponds to the spacing between the electrodes 12 and 13. The second embodiment therefore allows the second gap to be formed in the device so as to have a high linearity and a
5 highly uniform width (L).

Accordingly, the second embodiment is capable of reducing the local variations of the electron emission characteristic in the electron-emitting device caused due to the ununiformity of the width of the second gap
10 16 described above and the ununiformities of distances from the device electrodes 12 and 13 to the second gap in the device shown in Figs. 19A through 19D or Fig. 20. Furthermore, the second embodiment also exhibits an effect of the electron beam emission described
15 above, thereby being capable of enhancing an electron emitting efficiency of the device and remarkably reducing a variation or deterioration of the characteristic during driving of the device.

Furthermore, the manufacturing method of electron-emitting device according to the present invention
20 makes it unnecessary to use the electrically conductive film 14 which is electrically connected to the device electrodes or the "forming" to form the second gap 16 in the electrically conductive film which are required
25 for the conventional activation step, thereby simplifying a configuration of the device and reducing a number of steps. In other words, the manufacturing

method according to the present invention makes it possible to inexpensively and efficiently manufacture an electron-emitting device which has a stable and highly efficient electron emission efficiency.

5 Furthermore, the manufacturing method according to the present invention makes it possible to provide an electron source and an image-forming apparatus which comprise the electron-emitting device described above arranged in a plurality on a substrate, and have highly
10 uniform, highly efficient and stable characteristics.

At the activation step of the manufacturing method according to the present invention, in particular, it is preferable to apply the voltage to the device electrodes 12 and 13 while irradiating with the
15 electron beam from the electron emitting means 41 (51). In other words, it is preferable to perform an irradiation with the electron beam emitted from the electron emitting means while the voltage is applied to the device electrodes 12 and 13. This technique
20 permits enhancing a degree of crystallinity of the carbon and/or carbon compound which forms the first gap 17 at an initial stage of deposition. Speaking more concretely, compared with the conventional activation method, the carbon and/or carbon compound can be
25 deposited as a carbon film having a high degree of crystallinity from the initial stage of deposition by a current supplied between the device electrodes 12 and

13 since electrons having a high energy are projected
separately from the electron emitting means 41 (51).
Therefore, for example, it can be expected that the gap
17 is formed with a narrower width, thereby forming a
5 device having an excellent characteristic.

(Step E)

5) It is desirable to carry out an stabilization
step for an electron-emitting device obtained through
the activation step according to the present invention
10 described above. This step is carried out to exhaust
organic substances out of the vacuum vessel. For
evacuating the vacuum vessel, it is preferable to use a
vacuum evacuating apparatus which does not use an oil
so that the oil will not influence on a characteristic
15 of the device. Speaking concretely, a vacuum
evacuating apparatus such as a sorption pump, an ion
pump or the like can be used to evacuate the vacuum
vessel.

When an oil diffusion pump or a rotary pump is
20 used as an evacuating apparatus and an organic gas
deriving from an oil component coming from the pump is
used at the activation step described above, it is
necessary to suppress a partial pressure of this
component to a low level. It is preferable that a
25 partial pressure of an organic component in the vacuum
vessel is at a level not higher than 1×10^{-6} Pa at
which the carbon or carbon compound is scarcely

deposited newly and it is more preferable that the partial pressure is at a level not higher than 1×10^{-8} Pa in particular. At a stage to evacuate the vacuum vessel, it is preferable for to heat the vacuum vessel
5 as a whole to facilitate to evacuate molecules of the organic substances which are adsorbed by an inside wall of the vacuum vessel and the electron-emitting device. It is desirable to evacuate the vacuum vessel at 80 to 300°C, preferably at 150°C or higher, and for a time as
10 long as possible, but these conditions are not limitative and the vacuum vessel is evacuated in conditions adequately selected dependently on conditions such as a size and a shape of the vacuum vessel, a configuration of the electron-emitting device
15 and so on. It is necessary to evacuate the vacuum vessel to an extremely low level preferably not exceeding 1×10^{-5} Pa, more preferably not exceeding 1×10^{-6} Pa.

For driving after the stabilization step described
20 above, it is preferable to maintain the atmosphere which remains after termination of the stabilization step, but this atmosphere is not limitative and a stable characteristic can be maintained so far as the organic substances have been sufficiently eliminated
25 even when the pressure itself is more or less enhanced. By adopting such an atmosphere, it is possible to prevent the carbon or carbon compound from being newly

deposited, thereby stabilizing the device current I_f and the emission current I_e .

Now, description will be made of basic characteristics of the electron-emitting device according to the present invention. Fig. 5 is a schematic diagram showing an apparatus to evaluate the basic characteristics of the electron-emitting device according to the present invention. This evaluating apparatus has functions of not only an evacuating system but also of a device characteristic measuring system. In Fig. 5, members which are the same as those shown in Figs. 1A and 1B are denoted by reference numerals which are the same as those used in Figs. 1A and 1B. Describing concretely, reference numeral 11 denotes a substrate which composes an electron-emitting device, reference numerals 12 and 13 designate electrodes, reference numeral 14 denotes an electrically conductive film, and reference numeral 100 denotes an electron emitting region. The carbon film 15 is omitted for convenience. In addition, reference numeral 51 denotes a power source which applies a device voltage V_f to the electron-emitting device, reference numeral 50 designates an ammeter which measures a device current I_f supplied through the electrically conductive film 14 between the electrodes 12 and 13, and reference numeral 54 denotes an anode which captures the emission current I_e emitted from an

electron emitting region of the device. Reference numeral 53 denotes a high voltage power source which applies a voltage to the anode 54 and reference numeral 52 designates an ammeter which measures an emission
5 current I_e emitted from an electron emitting region 16 of the device. The basic characteristics of the device according to the present invention were measured while applying a voltage of 1 kV to the anode and reserving a distance H of 2 mm between the anode and the electron-
10 emitting device.

To measure the basic characteristics, a vacuum vessel is first evacuated to prevent carbon or a carbon compound from being newly deposited and a vacuum evacuating apparatus which does not use an oil, for
15 example a sorption pump, is used as a vacuum evacuating apparatus 56 to evacuate a vacuum vessel 55 so that an oil coming from an apparatus will not influence on the characteristics of the device.

A partial pressure of organic components in the
20 vacuum vessel 55 is set at a level not exceeding 1×10^{-8} Pa at which the carbon and carbon compound described above are not newly deposited. At this time, it is preferable to heat the vacuum vessel to 200°C or higher as a whole to facilitate to evacuate molecules
25 of organic substances which have been adsorbed by an inside wall of the vacuum vessel and the electron-emitting device.

Fig. 6 is a diagram schematically showing relationship among the emission current I_e , the device current I_f and the device voltage V_f of the electron-emitting device according to the present invention which were measured with the evaluating apparatus shown in Fig. 5. In Fig. 6, the emission current I_e is shown in an arbitrary unit since it is remarkably lower than the device current I_f .

As apparent also from Fig. 6, the electron-emitting device according to the present invention has three characteristic properties with regard to the emission current I_e as described below.

First, the electron-emitting device abruptly increases the emission current I_e when a device voltage exceeding a certain voltage level (referred to as a threshold voltage: V_{th} in Fig. 6), whereas the emission current I_e is scarcely emitted at a voltage level which does not exceed the threshold value voltage V_{th} . That is, the electron-emitting device according to the present invention is a non-linear device having the threshold voltage V_{th} which is clear relative to the emission current I_e .

Secondly, the emission current I_e can be controlled with the device voltage V_f since the emission current I_e increases monotonously with the device voltage V_f .

Thirdly, an amount of emitted electrons to be

captured by the anode 54 (see Fig. 5) is dependent on a time to apply the device voltage V_f . In other words, the amount of electrons to be captured by the anode 54 can be controlled by the time to apply the device
5 voltage V_f .

As understood from the foregoing description, the electron-emitting device according to the present invention has an electron emitting characteristic which can easily be controlled dependently on input signals.
10 By utilizing this property, the electron-emitting device according to the present invention is applicable to a variety of appliances such as an electron source and an image-forming apparatus which are composed by arranging a plurality of electron-emitting devices.

15 Though Fig. 6 shows an example wherein the device current I_f also increases monotonously with the device voltage V_f (hereinafter referred to as "MI characteristic"), the device current I_f may exhibit a voltage control type negative resistance characteristic
20 (hereinafter referred to as "VCNR characteristic") (not shown). These characteristics can be controlled by controlling the steps described above.

The electron-emitting device according to the present invention which has the characteristic
25 properties described above makes it possible to easily control an amount of emitted electrons in the electron source or the image-forming apparatus composed by

arranging a plurality of electron-emitting devices and can be applied to a variety of appliances.

Application examples of the electron-emitting device according to the present invention will be
5 described below. An electron source or an image-forming apparatus can be composed by arranging the electron-emitting device according to the present invention in a plurality on a substrate.

A variety of arrangements of electron-emitting
10 devices can be adopted. For example, there is a ladder type arrangement wherein a large number of electron-emitting devices are arranged in parallel and connected at ends on both sides, electron-emitting devices are arranged in a large number of lines (a line direction),
15 and electrons from the electron-emitting devices are controlled and driven with control electrodes (grid electrodes) which are disposed in a direction (a row direction) perpendicular to the line direction and above the above described electron-emitting device.
20 Separately from this arrangement, there is an arrangement wherein a plurality of electron-emitting devices are arranged in an X direction and a Y direction so as to form a matrix, a kind of electrodes of a plurality of electron-emitting devices arranged in
25 a line are connected commonly to wires in the X direction, and the other kind of electrodes of a plurality of electron-emitting devices are connected

commonly to wires in the Y direction. Such an arrangement is the so-called simple matrix arrangement. The simple matrix arrangement will be detailed below.

5 The electron-emitting device according to the present invention has the three characteristics as described above. Speaking concretely, electrons emitted from the electron-emitting device can be controlled with an amplitude and a width of a pulse voltage applied to the device electrodes opposed to
10 each other so far as the voltage exceeds the threshold voltage. While the voltage does not exceed the threshold voltage, on the other hand, electrons are scarcely emitted from the electron-emitting device. This characteristic makes it possible to select
15 electron-emitting devices and control an amount of emitted electrons dependently on input signals by applying an adequate pulse voltage to each of the electron-emitting device even when a large number of electron-emitting devices are arranged.

20 Referring to Fig. 12, description will be made of an electron source substrate which is obtained by arranging a plurality of the electron-emitting device according to the present invention. In Fig. 12, reference numeral 121 denotes an electron source
25 substrate, reference numeral 122 designates wires in the X direction, reference numeral 123 denotes wires in the Y direction. Reference numeral 124 denotes the

electron-emitting device according to the invention and reference numeral 125 designates a wiring.

The wires 122 which are arranged in a number of m in the X direction and consists of $Dx1, Dx2, \dots Dx_m$ can be composed of an electrically conductive metal or the like which are formed by the vacuum deposition method, printing method or sputtering process. A material, film thickness and width of the wires are designed adequately. The wires 123 which are arranged in a number of n in the Y direction consists of $Dy1, Dy2, \dots Dy_n$ and are formed similarly to the wires 122 in the X direction. Insulating layers (not shown) are formed between the m wires 122 in the X direction and the n wires 123 in the Y direction to electrically separate the wires 122 from the wires 123 (Both m and n are positive integers).

The insulating layers (not shown) are composed of SiO_2 or the like formed by the vacuum deposition method, printing method or sputtering process. The insulating layers are formed in a desired shape, for example, over an entire surface or portions of the substrate 121 on which the wires 122 are formed in the X direction, and thickness, a material and a manufacturing method of the layers are selected so that the layers are bearable of potential differences at intersections between the wires 122 in the X direction and the wires 123 in the Y direction. The wires 122 in the X direction and the

wires 123 in the Y direction are pulled out as external terminals, respectively.

Pairs of device electrodes (not shown) which compose the electron-emitting devices 124 are
5 electrically connected to the m wires 122 in the X direction and the n wires 123 in the Y direction via the wirings 125 made of an electrically conductive metal or the like.

All or some of component elements of materials
10 which are used to compose the wires 122 in the X direction, the wires 123 in the Y direction, the wirings 125 and the pairs of the device electrodes may be the same or different from one another. These materials are selected adequately, for example, from
15 among the materials for the device electrodes described above. When the material of the device electrodes is the same as that of the wires, the wires which are connected to the device electrodes may be said as the device electrodes.

20 The wires 122 in the X direction are connected to scanning signal applying means (not shown) which applies a scanning signal to select a line of the electron-emitting devices 124 arranged in the X direction. On the other hand, the wires 123 in the Y
25 direction are connected to a modulation signal generating means (not shown) which modulates each row of the electron-emitting devices 124 arranged in the Y

direction according to the input signal. A driving voltage is applied to each electron-emitting device as a differential voltage between the scanning signal and the modulation signal applied to the electron-emitting device.

The configuration described above makes it possible to select individual devices and drive the devices independently using a simple matrix wiring.

Referring to Figs. 13, 14 and 15, description will be made of an image-forming apparatus which is configured using an electron source with such a simple matrix arrangement. Fig. 13 is a schematic diagram showing an example of a display panel of the image-forming apparatus and Figs. 14A and 14B are schematic diagrams showing a fluorescent film used for the image-forming apparatus shown in Fig. 13. Fig. 15 is a block diagram exemplifying a driving circuit for display according to TV signals of an NTSC system. The members which are the same as those shown in Fig. 12 are denoted by the same reference numerals and not described in particular. The electrically conductive film 14 and the electrically conductive film 15 are omitted for convenience.

In Fig. 13, reference numeral 131 denotes a rear plate to which the electron source substrate 121 is fixed, and reference numeral 136 designates a face plate having a fluorescent film 134, a metal back 135

and so on which are formed on an inside surface of a glass substrate 133. Reference numeral 132 denotes a support frame to which the rear plate 131 and the face plate 136 are connected using fritted glass or the
5 like. Reference numeral 138 denotes an enclosure which is composed by bonding, for example within a temperature range from 400 to 500°C for 10 minutes or longer.

The enclosure 138 is composed of the face plate
10 136, the support frame 132 and the rear plate 131 as described above. Since the rear plate 131 is disposed mainly to reinforce the electron source substrate 121, the rear plate 131 is unnecessary when the substrate 121 itself has sufficient strength. Speaking
15 concretely, the support frame 132 may be sealed directly to the substrate 121, and the enclosure 138 may be composed of the face plate 136, the support frame 132 and the substrate 121. On the other hand, the enclosure 138 can be composed so as to have
20 sufficient strength to an atmospheric pressure by disposing a support member called a spacer (not shown) between the face plate 136 and the rear plate 131.

Figs. 14A and 14B are schematic diagrams showing a fluorescent film. A fluorescent film 134 can be
25 composed only of fluorescent materials when the film is monochromatic. A color fluorescent film can be composed of a black electrically conductive material

141 called black stripe (Fig. 14A) or black matrix (Fig. 14B) and fluorescent materials 142. The black stripe or the black matrix is disposed to make color mixtures not conspicuous by blackening coated borders among the fluorescent materials 142 of the three primary colors required for color display and prevent contrast from being lowered by external rays reflected by the fluorescent film 134. Usable as a material of the black electrically conductive material 141 is a substance which is electrically conductive and scarcely transmits or reflects rays in addition to a substance having graphite as a main component which is ordinarily used.

A deposition method, printing method or the like can be adopted to apply the fluorescent materials to the glass substrate 133 whether the film is monochromatic or colored. A metal back 135 is ordinarily disposed on an inside surface of the fluorescent film 134. Purposes to dispose the metal back is to enhance luminance by specular reflection toward the glass substrate 133 rays which travel toward the inside surface out of rays emitted from the fluorescent material, to make the rays as an electrode for application of an electron beam accelerating voltage, to protect the fluorescent material from damage due to bombardment of negative ions produced in the enclosure, and so on. The metal back can be

manufactured by carrying out a smoothing treatment
(generally called "filming") of the inside surface of
the fluorescent film after forming the fluorescent film
and then depositing Al by vacuum deposition or the
5 like.

Furthermore, the face plate 136 may contain a
transparent electrode (not shown) which is disposed on
an outside surface of the fluorescent film 134 to
enhance electrical conductivity of the fluorescent film
10 134.

In case of the color fluorescent film, it is
necessary to correspond the fluorescent material of
each color to each electron-emitting device and
sufficient positioning is indispensable at the sealing
15 stage described above.

The image forming apparatus shown in Fig. 13 is
manufactured, for example, as described below.

The enclosure 138 is sealed after its interior is
evacuated while adequately heating with an evacuating
20 apparatus such as the ion pump or the sorption pump
which does not use an oil like the evacuation at the
stabilization step described above until it is filled
with an atmosphere which is at a vacuum degree on the
order of 1×10^{-5} Pa and contains sufficiently little
25 organic substance. A getter treatment may be carried
out to maintain the vacuum degree after sealing the
enclosure 138. This is a treatment carried out to form

a deposited film, after immediately before or after sealing the enclosure 138, by heating a getter (not shown) disposed at a predetermined location in the enclosure 138 with a resistance heater or a high-
5 frequency heater. The getter ordinarily has a main component of Ba or the like and serves to maintain a high vacuum degree not lower than 1×10^{-5} Pa, for example, by an adsorbing function of the deposited film.

10 In the next place, description will be made of a configurational example of a driving circuit for TV display with the TV signals of the NTSC system on a display panel composed using the electron source of the simple matrix arrangement as shown in Fig. 15. In Fig.
15 15, reference numeral 151 denotes a display panel, reference numeral 152 designates a scanning circuit, reference numeral 153 denotes a control circuit, reference numeral 154 denotes a shift register, reference numeral 155 designates a line memory,
20 reference numeral 156 denotes a synchronizing signal separator circuit, reference numeral 157 denotes a modulating signal generator, and reference symbols V_x and V_a designate DC voltage sources.

The display panel 151 is connected to external
25 electric circuits via terminals $Dx1$ through Dxm , terminals $Dy1$ through Dyn and a high voltage terminal 137. Applied to the terminals $Dx1$ through Dxm are

scanning signals to drive an electron source disposed in the display panel 151, that is, to sequentially drive line by line (n devices) a group of electron-emitting devices which are wired in a matrix of m lines and n rows. Applied to the terminals Dyl through Dyn are modulating signals to control electron beams output from the electron-emitting devices in a line which is selected by the scanning signal. Supplied from the DC voltage source Va to the high voltage terminal 137 is a DC voltage, for example of 10 kV, which is an accelerating voltage to give the electron beam emitted from the electron-emitting device an energy sufficient to excite the fluorescent material.

Now, description will be made of the scanning circuit 152. This circuit comprises n switching elements (schematically denoted by S1 through Sm in Fig. 15). The switching elements select either an output voltage from the DC voltage source Vx or 0 [V] (ground level) and are electrically connected to the terminals Dx1 through Dxm on the display panel 151. The switching elements S1 through Sm operate on the basis of a control signal Tscan output from the control circuit 153 and can be composed, for example, by combining switching elements such as FETs.

On the basis of the characteristic of the electron-emitting device (the threshold value voltage for emission of electrons), the DC voltage source Vx is

set to output such a constant voltage as to keep a driving voltage applied to a device which is not scanned lower than the threshold value voltage for emission of electrons.

5 The control circuit 153 has a function to match operations of the members so that an image is displayed adequately on the basis of image signals input from outside. The control circuit 153 generates control signals Tscan, Tsft and Tmry for the members on the
10 basis of a synchronizing signal Tsync sent from the synchronizing signal separator circuit 156.

 The synchronizing signal separator circuit 156 is a circuit which separates a synchronizing signal component and a luminance signal component from the TV
15 signal of the NTSC system input from outside, and can be composed of a general frequency separator (filter) circuit. Though the synchronizing signal separated by the synchronizing signal separator circuit 156 consists
20 of a vertical synchronizing signal and a horizontal synchronizing signal, the synchronizing signal is denoted as Tsync herein for convenience of description. The luminance signal component of an image separated from the TV signal is designated as DATA signal for convenience. This DATA signal is input into the shift
25 register 154.

 The shift register 154 is used for serial/parallel conversion, per line of an image, of the DATA signals

described above which are input in time series and operates on the basis of the control signals Tsft sent from the control circuit 153 (in other words, it may be said that the control signal Tsft is a shift clock of
5 the shift register 154). Data of a line of the image subjected to the serial/parallel conversion (corresponding to driving data for n electron-emitting devices) is output from the shift register 154 as n parallel signals Id1 through Idn.

10 The line memory 155 is a memory which stores the data of a line of the image for a required time and stores contents of Id1 through Idn adequately according to the control signal Tmry sent from the control circuit 153. Stored contents are output as Id'1
15 through Id'n and input into the modulating signal generator 157.

The modulating signal generator 157 is a signal source which adequately drives and modulates each electron-emitting device in accordance with each image
20 data Id'1 through Id'n and output signals from the modulating signal generator 157 are applied to the electron-emitting devices in the display panel 151 via the terminals Dyl through Dyn.

As already described above, the electron-emitting
25 device according to the present invention has the following basic characteristics in the emission current Ie. That is, the electron-emitting device has the

clear threshold value voltage V_{th} for emission of electrons and emits electrons only when a voltage higher than V_{th} is applied. At a voltage higher than the threshold value for emission of electrons, the
5 emission current also varies dependently on variations of the applied voltage to the device. When a pulse voltage is applied to the electron-emitting device, the device therefor emits no electron when a voltage lower than the threshold value for emission of electrons is
10 applied, but the device emits an electron beam when a voltage higher than the threshold value for emission of electrons is applied. At this stage, it is possible to control an intensity of the output electron beam by changing the crest value V_m of pulses. Furthermore, it
15 is possible to control a total amount of electric charges of the output electron beam by changing the width P_w of the pulses.

Accordingly, a voltage modulation system, a pulse width modulation system and the like can be adopted as
20 a system to modulate the electron-emitting device dependently on input signal. To adopt the voltage modulation system, usable as the modulating signal generator 157 is a voltage modulation type circuit which generates voltage pulses having a definite length
25 and can adequately modulate the crest value of voltage pulses dependently on input data. To adopt the pulse width modulation system, usable as the modulating

signal generator 157 is a pulse width modulation type circuit which generates voltage pulses having a definite crest value and adequately modulates a width of the voltage pulses dependently on the input data.

5 The shift register 154 and the line memory 155 may be of a digital signal type or a analog signal type. This is because the shift register and the line memory are sufficient so far as these member performs the serial/parallel conversion and storage of the image
10 signals at predetermined speeds.

 When digital signal type shift register and line memory are used, it is necessary to convert the output signal DATA from the synchronizing signal separator circuit 156 into digital signals and it is sufficient
15 for this purpose to dispose an A/D converter in an output section of the synchronizing signal separator circuit 156. In relation to these signals, a circuit to be used as the modulating signal generator 157 is slightly different dependently on whether the line
20 memory 155 outputs digital signals or analog signals. In case of the voltage modulation system which uses digital signals, a D/A converter circuit, for example, is used as the modulating signal generator 157 and amplifier circuit, etc. are added as occasion demands.
25 In case of the pulse width modulation system, used as the modulating signal generator 157 is a circuit consisting of a combination, for example, of a

high-speed oscillator, a counter which counts wavenumbers output from the oscillator and a comparator which compares an output value from the counter with an output value of the memory. It is possible as occasion
5 demands to add an amplifier which performs voltage amplification of modulating signals which are modulated in pulse width and output from the comparator to the driving voltage for the electron-emitting device.

In case of the voltage modulation system which
10 uses the analog signals, an amplifier circuit which uses an operation amplifier or the like, for example, is used as the modulation signal generator 157 and a level shift circuit or the like can be added as occasion demands. In case of the pulse width
15 modulation system, a voltage control type oscillator circuit (VCO) can be adopted and an amplifier which performs voltage amplification to the driving voltage for the electron-emitting device can be added as occasion demands.

20 In the image-forming apparatus according to the present invention which can have the configuration described above, electrons are emitted by applying a voltage to the electron-emitting devices via the external terminals Dx1 through Dx_m and Dy1 through Dy_n
25 of the enclosure. Simultaneously, an electron beam is accelerated by applying a high voltage to the metal back 135 or the transparent electrode (not shown) via

the high voltage terminal 137. Accelerated electrons bombard the fluorescent film 134, which is glowed to form an image.

5 The configuration of the image-forming apparatus described above is an example of configuration of the image-forming apparatus according to the present invention and can be modified variously on the basis of the technique according to the present invention. Though the input signal of the NTSC system are
10 described above, the input signals are not limitative and it is possible to adopt signals of a PAL system, a SECAM system or other TV signals having scanning lines in a larger number (for example, those of a high-definition TV such as a MUSE system).

15 Now, description will be made of the electron source and the image-forming apparatus of the ladder type arrangement described above with reference to Figs. 16 and 17.

Fig. 16 is a schematic diagram exemplifying an
20 electron source of the ladder type arrangement. In Fig. 16, reference numeral 160 denotes an electron source substrate and reference numeral 161 designates electron-emitting devices. Reference numeral 162 denotes common wires D1 through D10 to connect the
25 electron-emitting devices 161 which are pulled out as external terminals. The electron-emitting devices 161 are arranged in a plurality in parallel in an X

direction on the substrate 160 (referred to as device lines). The device lines are arranged in a plurality to compose the electron source. The device lines can be driven independently by applying driving voltages to the common wires. Speaking concretely, a voltage higher than the threshold value voltage for emission of electrons is applied to a device line which is to emit an electron beam and a voltage lower than the threshold value voltage for emission of electrons is applied to a device line which is not to emit an electron beam. D2 and D3, for example, of the common wires D2 through D9 among the device lines can be integrated into a single wire.

Fig. 17 is a schematic diagram exemplifying a panel structure of an image-forming apparatus which comprises the electron source of the ladder type arrangement. Reference numeral 170 denotes grid electrodes, reference numeral 171 designates openings through which electrons pass, reference symbols D1 through Dm denote external terminals of a casing, reference symbols G1 through Gn denote external terminals of the casing which are connected to the grid electrodes 170. The reference numeral 160 designates the electron source substrate on which the common wires are integrated between the device lines. In Fig. 17, members which are the same as those shown in Figs. 13 and 16 are denoted by the same numerals and symbols.

The electrically conductive film 14 and the electrically conductive film 15 are omitted for convenience. Largely different from the image-forming apparatus of the simple matrix arrangement shown in Fig. 13, the image-forming apparatus shown in Fig. 17 comprises the grid electrodes 170 which are disposed between the electron source substrate 160 and the face plate 136.

In Fig. 17, the grid electrodes 170 are disposed between the substrate 160 and the face plate 136. The grid electrodes 170 function to modulate electron beams emitted from the electron-emitting devices 161 and have the openings 171 which are formed circular in stripe-shaped electrodes disposed perpendicular to the device lines of the ladder type arrangement to pass electron beams. Herein, there is one opening 171 for each device. A shape and arrangement of the grid electrodes are not limited to those shown in Fig. 17. It is possible, for example, to form a large number of mesh-like passage holes as the openings and dispose the grid electrodes around or in the vicinities of the electron-emitting devices.

The external terminals D1 through Dm and G1 through Gn of the casing are connected to a control circuit (not shown). Modulating signals for a line of an image are applied simultaneously to rows of the grid electrodes in synchronization with sequential scanning

of the devices line by line. Accordingly, the image-forming apparatus is capable of displaying the image line by line by controlling irradiation of the fluorescent material with each electron beam.

5 Then image-forming apparatus according to the present invention described above is usable not only as a display apparatus for TV broadcasting, TV conference system or a computer but also as an image-forming apparatus composed as an optical printer using a
10 photosensitive drum or the like.

 Fig. 18 is a block diagram showing an example of the image-forming apparatus according to the present invention which is configured to be capable of displaying image data provided from various image data
15 sources, for example, a TV broadcasting station.

 In Fig. 18, reference numeral 1700 denotes a display panel, reference numeral 1701 designates a drive circuit for the display panel, reference numeral 1702 denotes a display controller, reference numeral
20 1703 denotes a multiplexer, reference numeral 1704 designates a decoder, reference numeral 1705 denotes an input/output interface circuit, reference numeral 1706 denotes a CPU, reference numeral 1707 designates an image generating circuit, reference numerals 1708
25 through 1710 denote image memory interface circuits, reference numeral 1711 denotes an image input interface circuit, reference numerals 1712 and 1713 designate TV

signal receiving circuits, and reference numeral 1714 denotes an input unit.

When the image-forming apparatus receives signals such as TV signals containing both image data and voice data, for example, it reproduces voice while displaying an image as a matter of course, but description will not be made of circuits and a loudspeaker related to reception, separation, reproduction, processing, storage of the voice data which are not related directly to the characteristics of the present invention.

Now, description will be made of the circuits in a sequence of flows of image signals.

First, the TV signal receiving circuit 1713 is a circuit which receives TV signals transmitted, for example, through a radio transmission system such as a radio wave communication system or a spatial optical communication system. A system of the TV signals to be received is not limited in particular and may be, for example, the NTSC system, PAL system or the SECAM system. Furthermore, TV signals which consist of a larger number of scanning lines, for example, the so-called high-definition TV signals such as signals of the MUSE system are preferable to make use of merits of the display panel which is suited to have a large area and a large number of pixels.

The TV signals received by the TV signal receiving

circuit 1713 are output to the decoder 1704.

Furthermore, the TV signal receiving circuit 1712 is a circuit which receives TV signals transmitted through a wire-link transmission system such as a coaxial cable or an optical fiber. Like the TV signal receiving circuit 1713, the TV signal receiving circuit 1712 does not limit a system of TV signals to be received and the TV signals received by the TV signal receiving circuit 1712 are output also to the decoder 1704.

The image input interface circuit 1711 is a circuit which takes image signals supplied from an image input unit such as a TV camera or an image reading scanner and image signals taken by this interface circuit are output to the decoder 1704.

The image memory interface circuit 1710 is a circuit which takes image signals stored in a video tape recorder (hereinafter referred to as "VTR") and image signals taken by this circuit are output to the decoder 1704.

The image memory interface circuit 1709 is a circuit which takes image signals stored in a video disk and image signals taken by this circuit are output to the decoder 1704.

The image memory interface circuit 1708 is a circuit which takes image signals from a unit which stores still image data like a still image disk and

still image data taken by this circuit is input into the decoder 1704.

The input/output interface circuit 1705 is a circuit which connects the image-forming apparatus to an external output apparatus such as a computer, a computer network or a printer. This circuit is capable of inputting and outputting image data and character/figure data, and may allow input and output of control signals and numerical data between the CPU 1706 of the image-forming apparatus and an external apparatus.

The image generating circuit 1707 is a circuit which generates image data to be displayed on the basis of image data and character/figure data which are input from outside via the input/output interface circuit 1705 and image data and character/figure data which are output from the CPU 1706. Built in the image generating circuit 1707 are circuits which are necessary to generate images such as a rewritable memory for accumulating the image data and the character/figure data, a read only memory for storing image patterns corresponding to character codes and a processor for image processing.

Image data to be displayed which is generated by this circuit is output to the decoder 1704 and can be output, in a certain case, to the external computer network or printer via the input/output interface

circuit 1705 described above.

The CPU 1706 mainly controls operations of the image-displaying apparatus and performs works related to generation, selection and edition of images to be
5 displayed.

For example, the CPU 1706 outputs control signals to the multiplexer 1703, and adequately selects and combines image signals to be displayed on the display panel. At this stage, the CPU 1706 generates control
10 signals for the display panel controller 1702 according to the image signals to be displayed, thereby adequately controlling operations of a display unit such as a screen display frequency, a scanning mode (for example, interlace or non-interlace) and a number
15 of scanning lines on a screen. Furthermore, the CPU 1706 outputs the image data and character/figure data directly to the image generating circuit 1707, and makes access to the external computer or memory via the input/output interface circuit 1705 to input the image
20 data and character/figure data.

In addition, the CPU 1706 may relates to works for other purposes. For example, it may have direct relation to a data generating function and a data
processing function like a personal computer or a word
25 processor. Alternately, the CPU 1706 may be connected to the external computer network via the input/output interface circuit 1705 so that the CPU performs works

such as numerical calculations, for example, in cooperation with external equipment.

The input unit 1714 is operated by a user to input programs or data into the CPU 1706 and usable as the
5 input unit 1714 is various input appliances, for example, not only a keyboard and a mouse but also a joystick, a bar code reader and a voice recognizer.

The decoder 1704 is a circuit which converts various image signals input from the image memory
10 interface circuits 1707 through 1713 described above reversely into signals of the three primary colors or luminance signals, I signals and Q signals. It is desirable that the decoder 1704 comprises an image memory as indicated by a chain line in Fig. 18. An
15 image memory is disposed to process TV signals such as those of the MUSE system which require an image memory for reverse conversion. Furthermore, an image memory facilitates to display a still image. An image memory provides merit to facilitate to perform image
20 processings and edition such as omission, supplementation, expansion, contraction and synthesis of images as well as edition of images in cooperation with the image generating circuit 1707 and the CPU 1706.

25 The multiplexer 1703 adequately selects images to be displayed on the basis of control signals input from the CPU 1706. Speaking concretely, the multiplexer

1703 selects desired image signals out of the reversely converted image signals which are input from the decoder 1704 and outputs selected image signal to the drive circuit 1701. At this stage, the multiplexer
5 1703 is capable of selecting the image signals while switching the image signals within a display time for a scene so that the screen is divided into a plurality of regions and different images are displayed on the regions as those on the so-called multi-screen TV.

10 The display panel controller 1702 is a circuit which controls operations of the drive circuit 1701 on the basis of control signals input from the CPU 1706 described above.

In relation to basic operations of the display
15 panel, signals to control an operating sequence of a driving power source (not shown) for the display panel, for example, are output to the drive circuit 1701. In relation to a driving method of the display panel, signals to control the screen display frequency and a
20 scanning mode (for example, the interlace or non-interlace), for example, are output to the drive circuit 1701. Furthermore, control signals related to adjustment of image qualities such as luminance, color tones or sharpness of the images to be displayed
25 contrast, may be output to the drive circuit 1701.

The drive circuit 1701 is a circuit which generates driving signals to be applied to the display

panel 1700, and operates on the basis of the image signals input from the multiplexer 1703 described above and the control signals input from the display panel controller 1702 described above.

5 With the circuits having the functions described above, the image-forming apparatus which has the configuration shown in Fig. 18 is capable of displaying image data input from various image data sources on the display panel 1700. Speaking concretely, various kinds
10 of image signals such as those of TV broadcasting are reversely converted by the decoder 1704, selected adequately by the multiplexer 1703 and input into the drive circuit 1701. On the other hand, the display controller 1702 generates control signals to control
15 the operations of the drive circuit 1701 dependently on the image signals to be displayed. The drive circuit 1701 applies the driving signals to the display panel 1700 on the basis of the image signals described above and the control signals. Accordingly, the display
20 panel displays an image. A series of these operations are controlled collectively by the CPU 1706.

 The image-forming apparatus is capable of not only displaying data selected from the data in the image memory built in the decoder 1704 and the image
25 generating circuit 1707 described above, but also, for the image information to be displayed, performing image processings such as the expansion, contraction,

rotation, movement, edge emphasis, omission,
supplementation, color conversion and aspect ratio
conversion of images as well as edition such as
synthesis, erasion, connection, exchange and fitting of
5 images. Furthermore, circuits exclusively for
processing and edition of voice data may also be
disposed like those for the image processing and the
image edition.

Accordingly, the image-forming apparatus can have
10 collective functions usable as a display appliance for
TV broadcasting, a terminal appliance for TV
conferences, an image edition appliance to process
still images and moving images, a terminal appliance
for a computer, a business terminal appliance such as a
15 word processor and a game appliance, thereby being
applicable widely in industrial fields and for purposes
of public welfare.

Fig. 18 shows only an example of a case wherein
the image-forming apparatus uses the display panel
20 which is composed of the electron-emitting devices as
an electron beam source and it is needless to say that
the image-forming apparatus according to the present
invention is not limited to that shown in Fig. 18.

It is allowed to omit, for example, circuits which
25 are not related to purposes unnecessary for purposes of
use out of component members shown in Fig. 18.

Reversely, additional component members may be used

dependently on purposes of use. When the image-forming apparatus is to be used as a TV telephone, for example, it is preferable to add a transception circuit which comprises a TV camera, voice microphone, an illuminator
5 and a modem.

The image-forming apparatus which uses the electron-emitting devices as the electron source facilitates to thin a display panel and can have a reduced depth of the image-forming apparatus. In
10 addition, the display panel which uses the electron-emitting devices as the electron beam can easily have a large screen, high luminance and a large angle of view, whereby the image-forming apparatus is capable of displaying an image which is full of a feeling of
15 presence and high appealing power with good legibility.

(Example 1)

An electron-emitting device which has the configuration shown in Figs. 1A and 1B was manufactured as Example 1 of the present invention. Example 1 will
20 be described with reference to Figs. 1A, 1B and 2A through 2D. Silica glass was used as the substrate 11, and Pt was used as a material of the device electrodes taking stability to humidity and stability to oxidation into consideration. Furthermore, thickness of the
25 electrically conductive film 14 was set at 30 nm taking a resistance value between the device electrodes 12 and 13 into consideration. L was 20 μm , W was 100 μm and

film thickness d was 10 nm in Example 1.

The electrically conductive film 14 was formed by coating the substrate 11 disposed the electrodes 12 and 13 with an organic Pd solution ("ccp-4230" prepared by
5 Okuno Chemical Industries Co., Ltd.) to form an organometal film, heating the film for calcination and patterning the film (Figs. 2A and 2B).

Then, a triangular wave pulse shown in Fig. 3 was applied repeatedly with a pulse height kept constant.
10 Pulse width T_1 and pulse interval T_2 shown in Fig. 3 were set at 100 μ sec and 1 msec respectively, and the amplitude of the triangular wave was set at 10 V. In these conditions, the second gap 16 was formed by applying a pulse voltage for 600 seconds (Fig. 2C).

15 Then, the device described above was subjected to the activation treatment. Speaking concretely, a substrate on which the device was formed was placed in the apparatus shown in Fig. 4, acetone was introduced as an organic substance gas into sufficiently evacuated
20 vacuum with an ion pump or the like and maintained at 1×10^{-5} Pa, and the voltage was applied to the electrodes (12, 13) with a triangular wave pulse which was the same as that for forming the second gap 16 and irradiated with an electron beam at an accelerating
25 voltage of 20 kV. However, a pulse width, a pulse interval and a pulse height of the triangular wave pulse were set at 1 msec, 10 msec and 15 V respectively.

The activation treatment, that is, the forming step of the carbon films 15, was carried out until the predetermined device current I_f was reached.

Transmission electron microscopy of a section of an
5 obtained device indicated film thickness of 50 nm in the vicinity of the gap 17. In addition, the carbon films 15 were opposed to each other with the first gap 17 interposed as shown in Fig. 2D. Furthermore, the first gap 17 was narrower than the second gap 16 and
10 disposed in the second gap 16. Furthermore, Raman spectroscopy indicated that the carbon films 15 contained a graphite structure and had a high crystallization.

Furthermore, it was found out that no region
15 having high resistance did not exist in the carbon films 15 as a result of observation through an interatomic force/tunnel microscope having an interatomic force microscope probe which was made electrically conductive so that an electrical
20 conductivity distribution of a sample could be measured with the sample kept in contact with the probe. Furthermore, the probe was kept in contact with the carbon films 15 disposed on the electrically conductive film 14 during the measurement. An evaluation of
25 specific resistance in a direction of width of the film provided a result not higher than 0.001 Ωm . Comparison of this value with that of a carbon film 15 which was

formed without irradiation with electrons indicated a variation exceeding a place.

The device substrate described above was placed in the evaluating apparatus shown in Fig. 5 and its
5 electron emission efficiency was measured by applying a voltage of 1 kV to an anode with the distance H between the anode and the electron-emitting device set at 2 mm.

First, the organic substance gas was evacuated from the vacuum vessel 55 to prevent carbon or a carbon
10 compound from being newly deposited. A sorption pump was used as the vacuum evacuating apparatus 56 which evacuates the vacuum vessel 55 without using oil so that oil coming from the apparatus would not influence on the characteristic of the device. A partial
15 pressure of an organic component in the vacuum vessel 55 was adjusted to a level not exceeding 1×10^{-8} Pa at which carbon or the carbon compound is newly deposited scarcely. At this stage, the vacuum vessel is heated as a whole at a temperature not lower than 200°C to
20 facilitate to exhaust molecules of the organic substance adsorbed by an inside wall of the vacuum vessel and the electron-emitting device.

As a result, relationship between the device current I_f and the emission current I_e shown in Fig. 6
25 was obtained. Furthermore, an electron emission efficiency η was defined as a ratio of I_e relative to I_f with V_f and V_a fixed to 15 V and 1 kV respectively

and variations of η with time were measured in a condition where electrons are emitted.

As a result, an initial electron emission efficiency was enhanced 0,05% or more. Furthermore,
5 the variations of η with time were remarkably suppressed as compared with those of the electron-emitting device which was manufactured by the conventional manufacturing method. The conventional device exhibited enhancement of η at a ratio of
10 0.01%/1000h (h denotes hours) in a case where initial η was 0.1%, whereas the electron-emitting device manufactured by the method according to the present invention suppressed a variation ratio of η below 1/5.

(Example 2)

15 As Example 2 of the present invention, an electron source which has the configuration shown in Figs 7A and 7B was manufactured through the activation step shown in Figs. 9A and 9B.

In Example 2, basical configuration, materials and
20 a manufacturing method were the same as those in Example 1, but L1, W and film thickness of an electrode was set at 5 μm , 100 μm and 10 nm respectively. Furthermore, width L2 of the common device electrode was set at 5 μm .

25 An electron-emitting device was formed through steps similar to those in Example 1 before formation of an electron emitting region. Then, the activation

treatment was carried out by applying a pulse voltage in Figs. 8A and 8B across the device electrodes 73 and 74 with the common device electrode set at a ground potential. In Example 2, acetone was introduced as an organic substance and kept at 1×10^{-5} Pa. The pulse width t_1 , the pulse voltage and the pulse interval t_2 were set at 1 msec, 15 V and 200 msec respectively as conditions for applying the pulse voltage. Formation of the electrically conductive films 76 and 78 was continued until the device current I_f reached the predetermined level.

Transmission electron microscopy of a device thus obtained indicated that the carbon films 76 and 78 had thickness of 50 nm in the vicinities of the first gap 17 which composed the electron emitting region. Observations by the transmission microscopy and Raman spectroscopy of the obtained electron-emitting device indicated that the carbon films 76 and 78 contained graphite structures and had a high crystallization.

Furthermore, it was found out that no region having high resistance did not exist in the carbon films 76 and 78 as a result of observation through an interatomic force/tunnel microscope having a probe of an interatomic force microscope which was made electrically conductive as in Example 1 so that the microscope can measure an electrical conductivity distribution of a sample. Furthermore, an evaluation

of specific resistance in a direction of width provided a result not exceeding $0.0001 \Omega m$. Comparison of this value with that measured in a case where carbon films are formed without irradiation with electrons indicated
5 a variation exceeding two places.

The electron-emitting device which was formed as described above was placed in the evaluating apparatus shown in Fig. 5 and its electron emission efficiency was checked. However, drive was effected only on an
10 electron emitting region. The common device electrode was set at a high potential so that electrons were emitted always toward the common device electrode. Defining an electron emission efficiency η as a ratio of I_e relative to I_f , variations of η with time were
15 measured in a condition where electrons are emitted with V_f and V_a fixed to 15 V and 1 kV respectively.

As a result, an initial electron emission efficiency was first enhanced 0.1% or more. Furthermore, the electron-emitting device remarkably
20 suppressed the variations of η with time as compared with those of the electron-emitting device manufactured by the conventional manufacturing method. The conventional device exhibited enhancement of η at a ratio of 0.01%/1000h (h denotes hours) in a case where
25 initial η was 0.1%, whereas the electron-emitting device manufactured by the manufacturing method according to the present invention suppressed a

variation ratio η below 1/10.

(Example 3)

In Example 3, an electron-emitting device having the configuration shown in Figs. 21A and 21B was
5 manufactured. Example 3 will be described with reference to Figs. 21A, 21B, 22A, 22B and 23. Quartz was used as the substrate 11, and Pt was used as a material for the device electrodes 12 and 13 taking stability to humidity and stability to oxidation into
10 consideration.

Then, the activation process was effected on the device.

Speaking concretely, a substrate on which the device electrodes 12 and 13 were formed was placed in
15 the apparatus shown in Fig. 23, acetone was introduced as an organic substance gas into vacuum sufficiently evacuated with an ion pump or the like and maintained at 1×10^{-5} Pa, and pulses shown in Fig. 8A were applied across the electrodes 12 and 13. T_1 and t_2 shown in
20 Fig. 8A were set at 1 msec and 10 msec respectively. Simultaneously, the substrate was irradiated with an electron beam with an accelerating voltage set at 2 kV.

Forming step of the carbon film 15 was carried out until the device current I_f reached the predetermined
25 level. Observation by the transmission electron microscopy of a device obtained indicated that the first gap 17 was formed between the device electrodes

12 and 13 as shown in Figs 21A and 21B, and that the carbon film 15 was formed continuously over the electrodes 12 and 13. The gap 17 was located near in the middle between the electrodes 12 and 13.

5 Furthermore, observation by Raman spectroscopy provided a result that the carbon film 15 contains a graphite like layer structure and had high crystallization.

The electron-emitting device was placed in the evaluating apparatus shown in Fig. 5 and its electron
10 emission efficiency was measured with an anode voltage kept by 1 kV and with the distance H between the anode and the electron-emitting device set at 2 mm.

First, the organic substance evacuated from the vacuum vessel to prevent carbon or a carbon compound
15 from being newly deposited. In order to prevent the characteristic of the device from being influenced by oil coming from an apparatus, a sorption pump which used no oil was adopted as the vacuum evacuating apparatus 66 for evacuating the vacuum vessel 65. A
20 partial pressure of an organic compound in the vacuum vessel 65 was adjusted to a level not exceeding 1×10^{-8} Pa at which carbon or the carbon compound is newly deposited scarcely. At this stage, the vacuum vessel was heated as a whole at 200°C or higher to facilitate
25 to evacuate molecules of the organic substance adsorbed by an inside wall of the vacuum vessel and the electron-emitting device.

As a result, relationship between the device current I_f and the emission current I_e shown in Fig. 6 was obtained. Defining an electron emission efficiency η as a ratio of I_e relative to I_f , initial values of I_f , I_e and η , variations of the initial values and variations of the initial values with time were measured with in a condition where electrons are emitted with V_f and V_a kept fixed to 15 V and 1 kV respectively.

10 (Example 4)

In Example 4, the image-forming apparatus 138 shown in Fig. 13 was manufactured by the method described in Example 3. In addition, the substrate 121 served also as the rear plate 131.

15 First, 500 pairs of the device electrodes 12 and 13 and 1000 pairs of the device electrodes 12 and 13 were formed in the X direction and the Y direction respectively on the glass substrate 121 by an offset printing method (Fig. 24A). Successively, 500 wires
20 122 to be connected to the electrodes 12 were formed in the X direction by a screen printing method (Fig. 24B). 1000 insulating layers 124 were formed in a direction substantially perpendicular to the X direction by the screen printing method (Fig. 24C). 1000 wires were 123
25 formed in the Y direction on the insulating layers 124 so that the wires are connected to the electrodes 13 (Fig. 25D). As in Example 3, the carbon film 15 was

formed as shown in Fig. 23 by applying a voltage across the device electrodes 12 and 13 while irradiating a portion between the device electrodes 12 and 13 with an electron beam like a DC voltage from the electron emitting means 51 (Figs. 25E and 23). An electron source was formed through processes described above.

Successively, the electron source was positioned to the face plate 136 on which the fluorescent material 142 is arranged as an image forming member as shown in Fig. 14A, and the outer frame 132 having a preliminarily disposed joining member was disposed between the electron source and the face plate and sealed by heating and pressing the frame in the atmosphere of vacuum.

The image-forming apparatus 138 was manufactured through the processes described above.

When the image-forming apparatus was connected to the drive circuit shown in Fig. 15 and driven, it was capable of displaying an image having high luminance and uniformity stably for a long time.

(Example 5)

In Example 5, the image-forming apparatus 138 shown in Fig. 13 was manufactured by the manufacturing method in Example 1. In addition, in Example 5, the substrate 121 served also as the rear plate 131.

First, 500 pairs of the device electrodes 12 and 13 and 1000 pairs of the device electrodes 12 and 13

were formed in the X direction and the Y direction respectively on the glass substrate 121 by the offset printing method (Fig. 24A). Successively, 500 wires 122 to be connected to the electrodes 12 were formed in the X direction by the screen printing method (Fig. 24B). 1000 insulating layers 124 were formed in a direction substantially perpendicular to the X direction by the screen printing method (Fig. 24C). 1000 wires 123 were formed in the Y direction on the insulating layers 124 so that the wires are connected to the electrodes 13 (Fig. 26D). The electrically conductive film 14 was formed between the device electrodes 12 and 13 by an ink-jet method (Fig. 26E). As in Example 1, the second gap 16 was formed in a portion between the device electrodes 12 and 13 at the forming step by applying a voltage to the device electrodes 12 and 13 (Fig. 26F). The carbon film 15 was formed as shown in Figs. 2A through 2D and Fig. 4 by applying a voltage to the device electrodes 12 and 13 while irradiating a portion between the device electrodes 12 and 13 an electron beam like a DC voltage from the electron emitting means 51. An electron beam source was manufactured through the processes described above.

Successively, the electron beam was positioned to the face plate 136 on which the fluorescent material 142 is disposed as an image forming member as shown in

Fig. 14A, and the outside frame 132 having a
preliminarily disposed joining member was arranged
between the electron source and the face plate and
sealed by heating and pressing the frame in the
5 atmosphere of vacuum.

The image-forming apparatus 138 was manufactured
through the processes described above.

When the image-forming apparatus was connected to
the drive circuit shown in Fig. 15 and driven, the
10 apparatus was capable of displaying a highly luminant
and uniform image stable for a long time.

The manufacturing method of an electron-emitting
device according to the present invention is capable of
forming a carbon film which has low resistance and high
15 uniformity since the method permits forming the carbon
film having carbon as a main component while
irradiating it with sufficient electrons. Accordingly,
the manufacturing method according to the present
invention enhances an initial electron emission
20 efficiency and restrain physical properties of the
carbon film from being changed even when the carbon
film is irradiated with electrons emitted from an
electron emitting region during driving, thereby making
it possible to manufacture an electron-emitting device
25 which is free from variations of the electron emission
efficiency.

Accordingly, the present invention makes it

possible to provide an electron source having a high, stable and uniform electron emission efficiency, and to manufacture a highly luminant and reliable image-forming apparatus using the electron source.

WHAT IS CLAIMED IS:

1. A manufacturing method of an electron-emitting device comprising the steps of:

disposing an electrically conductive member having
5 a second gap on a substrate; and

applying a voltage to said electrically conductive member while irradiating at least said second gap with an electron beam from electron emitting means disposed apart from said electrically conductive member in an
10 atmosphere comprising a carbon compound.

2. A manufacturing method of an electron-emitting device comprising the steps of:

disposing first and second electrically conductive
15 members on a substrate with a second gap interposed;
and

applying a voltage to said first and second electrically conductive members while irradiating at least said second gap with an electron beam from
20 electron emitting means disposed apart from said electrically conductive members in an atmosphere comprising a carbon compound.

3. A manufacturing method of an electron-emitting
25 device comprising the steps of:

disposing an electrically conductive member having a second gap on a substrate; and

irradiating at least said second gap with an
electron beam from electron emitting means disposed
apart from said electrically conductive member in an
atmosphere comprising a carbon compound within a period
5 where a voltage is applied to said electrically
conductive member.

4. A manufacturing method of an electron-emitting
device comprising the steps of:

10 disposing first and second electrically conductive
members on a substrate with a second gap interposed;
and

irradiating at least said second gap with an
electron beam from electron emitting means disposed
15 apart from said electrically conductive members in an
atmosphere comprising a carbon compound within a period
where a voltage is applied to said first and second
electrically conductive members.

20 5. The manufacturing method of an electron-
emitting device according to claim 1 or 3, wherein said
electrically conductive member having said second gap
is an electrically conductive film which connects a
pair of electrodes to each other and has said second
25 gap in a portion of the electrically conductive film.

6. The manufacturing method of an

electron-emitting device according to claim 2 or 4,
wherein said electrically conductive members are a pair
of electrodes which are disposed with said second gap
interposed.

5

7. The manufacturing method of an electron-
emitting device according to claim 2 or 4, wherein said
electrically conductive members are a first
electrically conductive film and a second electrically
10 conductive film which are connected to a first and
second electrodes apart disposed respectively and are
disposed with said second gap interposed.

8. The manufacturing method of an electron-
15 emitting device according to any one of claims 1
through 4, wherein said applied voltage is a pulse like
voltage.

9. The manufacturing method of an electron-
20 emitting device according to any one of claims 1
through 4, wherein said electron beam is at an energy
level not lower than 1 keV and not higher than 20 keV.

10. A manufacturing method of an electron source
25 having a plurality of electron-emitting devices,
wherein said electron-emitting device is manufactured
by the manufacturing method according to any one of

claims 1 through 4.

11. A manufacturing method of an image-forming
apparatus having an electron source and an image
5 forming member, wherein said electron source is
manufactured by the manufacturing method according to
claim 10.

12. An electron-emitting device having a carbon
10 film, wherein said carbon film has specific resistance
not higher than 0.001 Ωm .

13. An electron source having a plurality of
electron-emitting devices, wherein said electron-
15 emitting device is the electron-emitting device
according to claim 12.

14. An image-forming apparatus having an electron
source and an image forming member, wherein said
20 electron source is the electron source according to
claim 13.

ABSTRACT OF THE DISCLOSURE

An electron-emitting device having favorable electron emitting characteristic stable for a long time, which is manufactured by a method comprising the

5 steps of disposing an electrically conductive member having a second gap on a substrate, and applying a voltage to the electrically conductive member while irradiating at least the second gap with an electron beam from electron emitting means disposed apart from

10 the electrically conductive member in an atmosphere comprising a carbon compound.

FIG. 1A

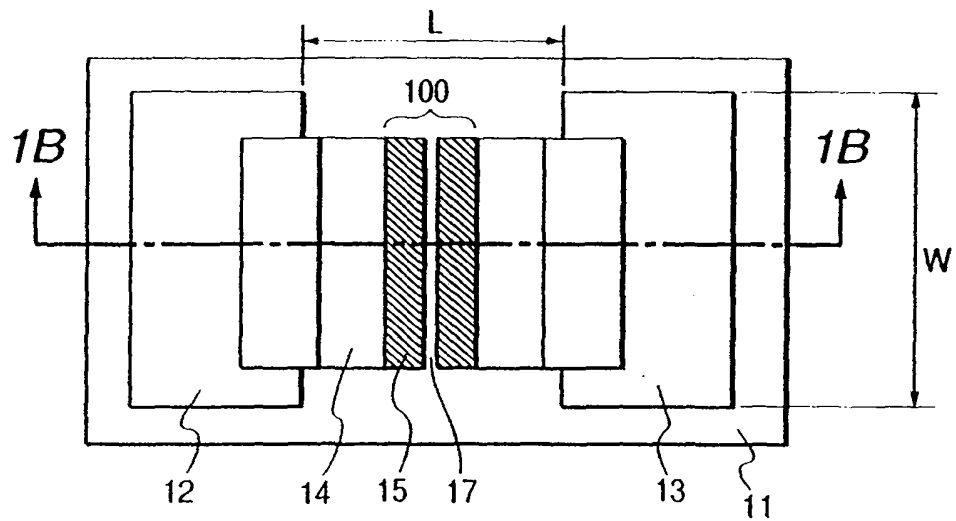


FIG. 1B

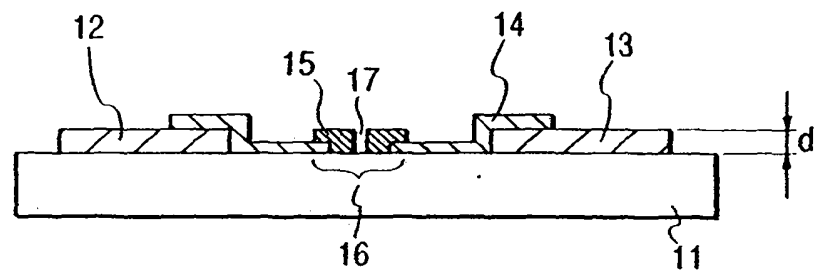


FIG. 2A

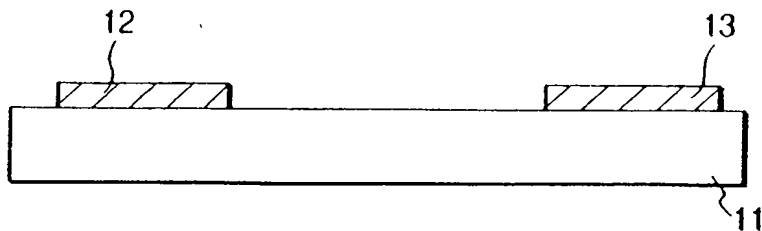


FIG. 2B

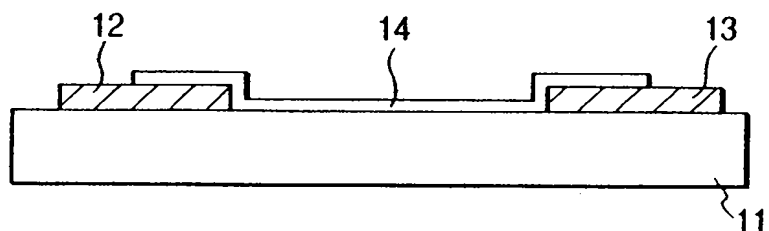


FIG. 2C

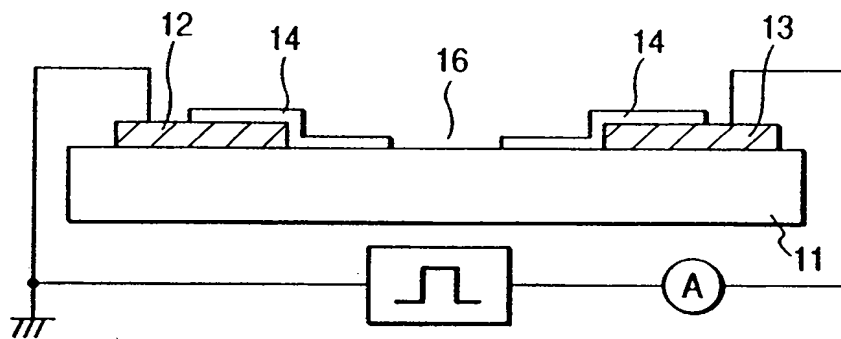


FIG. 2D

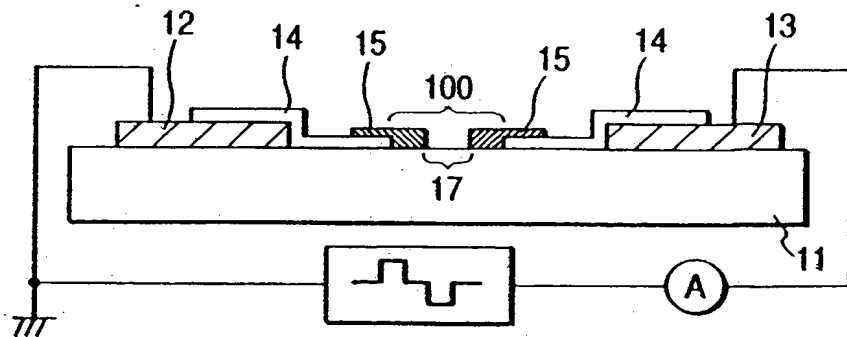


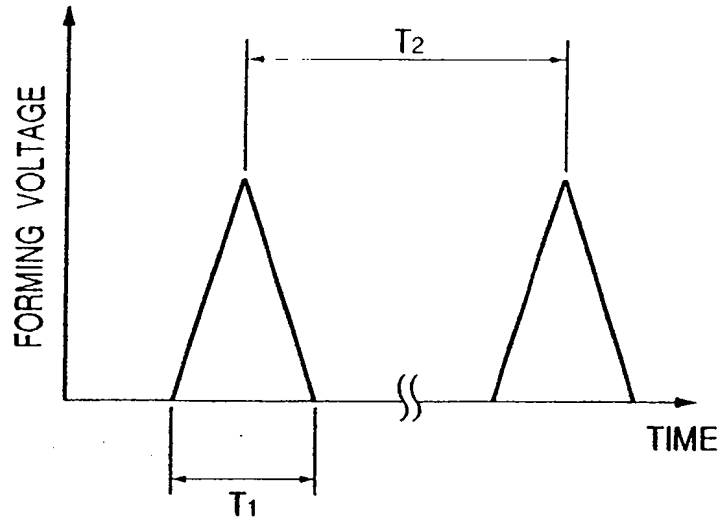
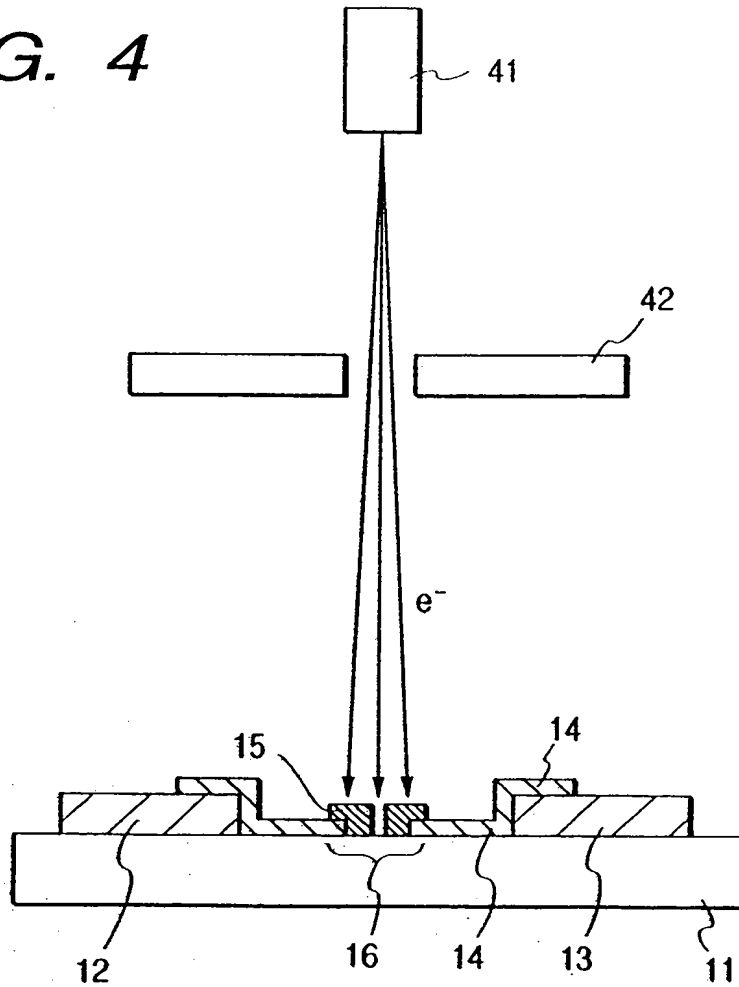
FIG. 3**FIG. 4**



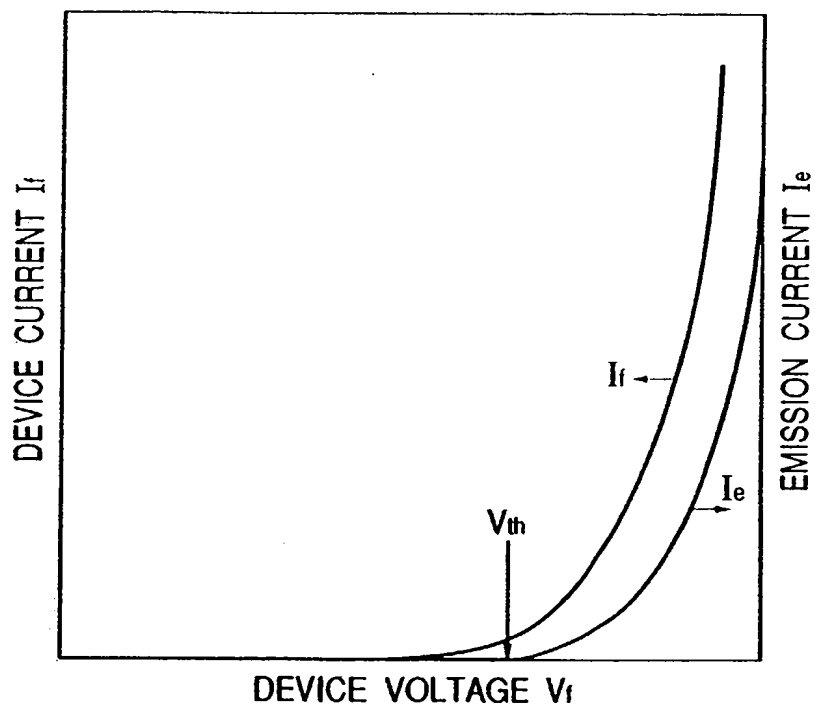
FIG. 6



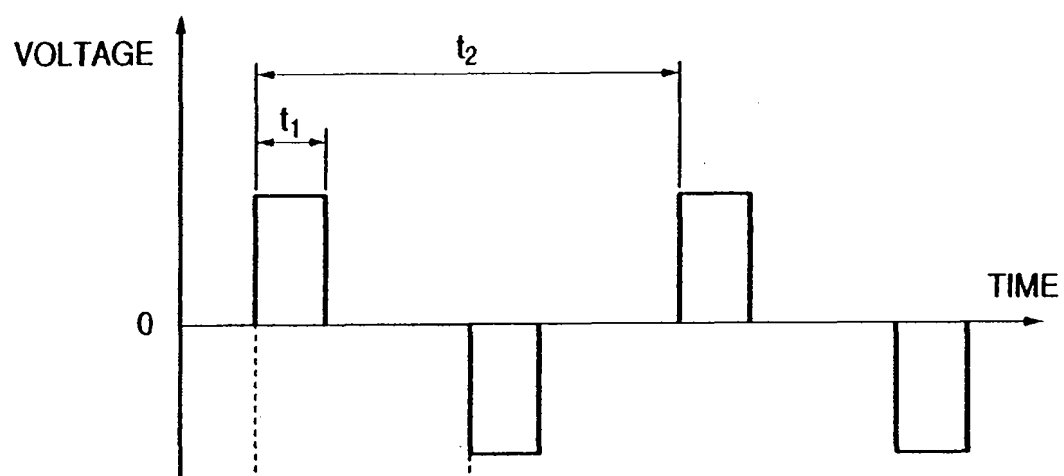
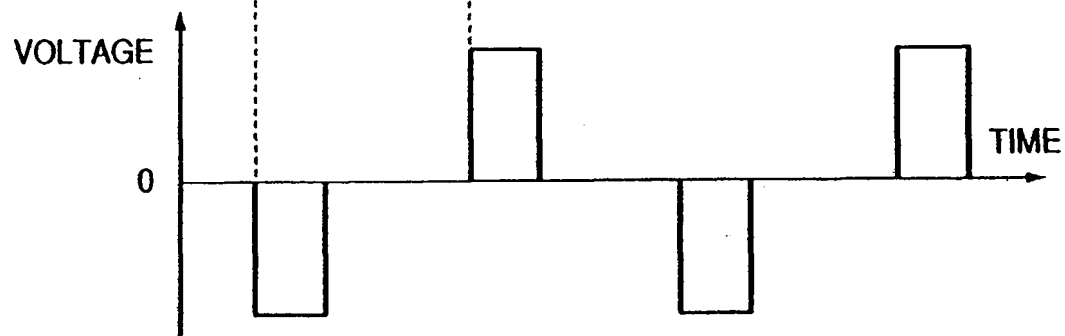
FIG. 8A*FIG. 8B*

FIG. 9A

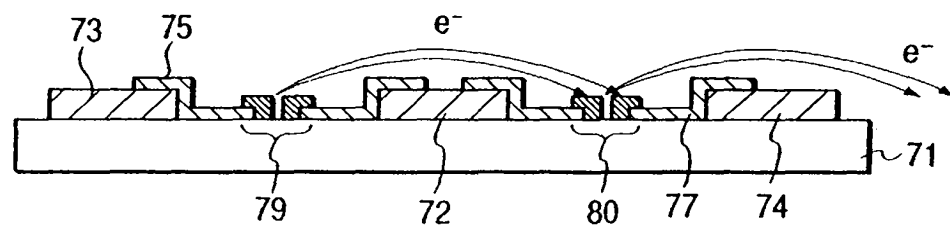


FIG. 9B

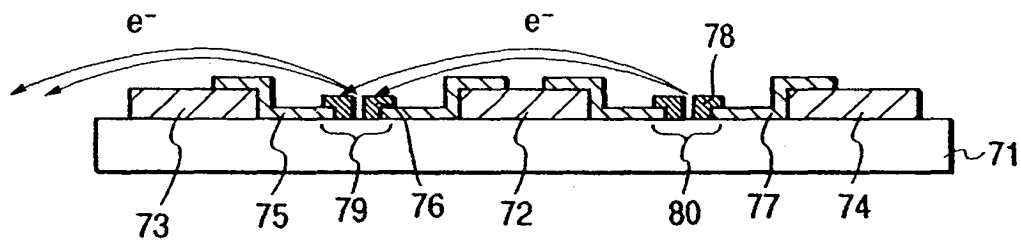


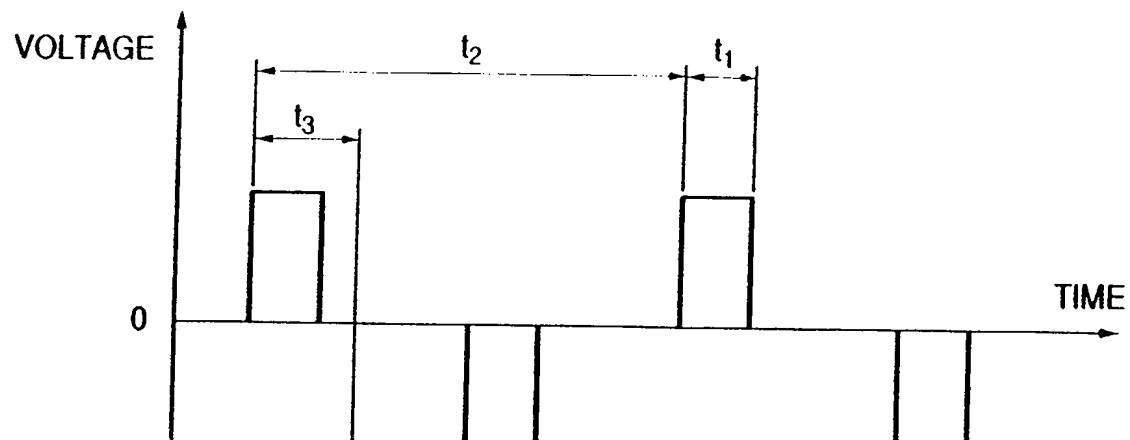
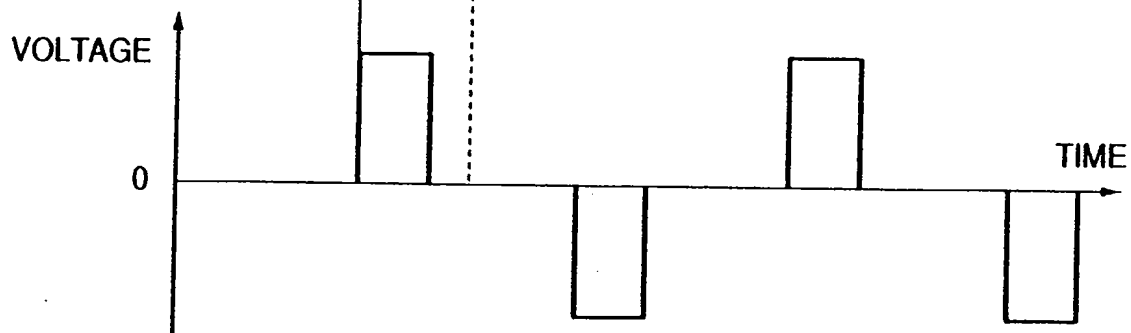
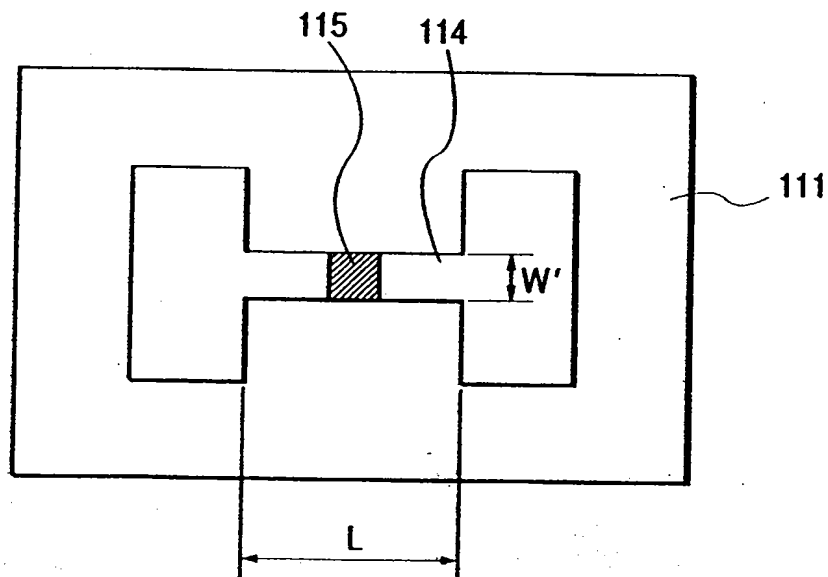
FIG. 10A**FIG. 10B****FIG. 11**

FIG. 12

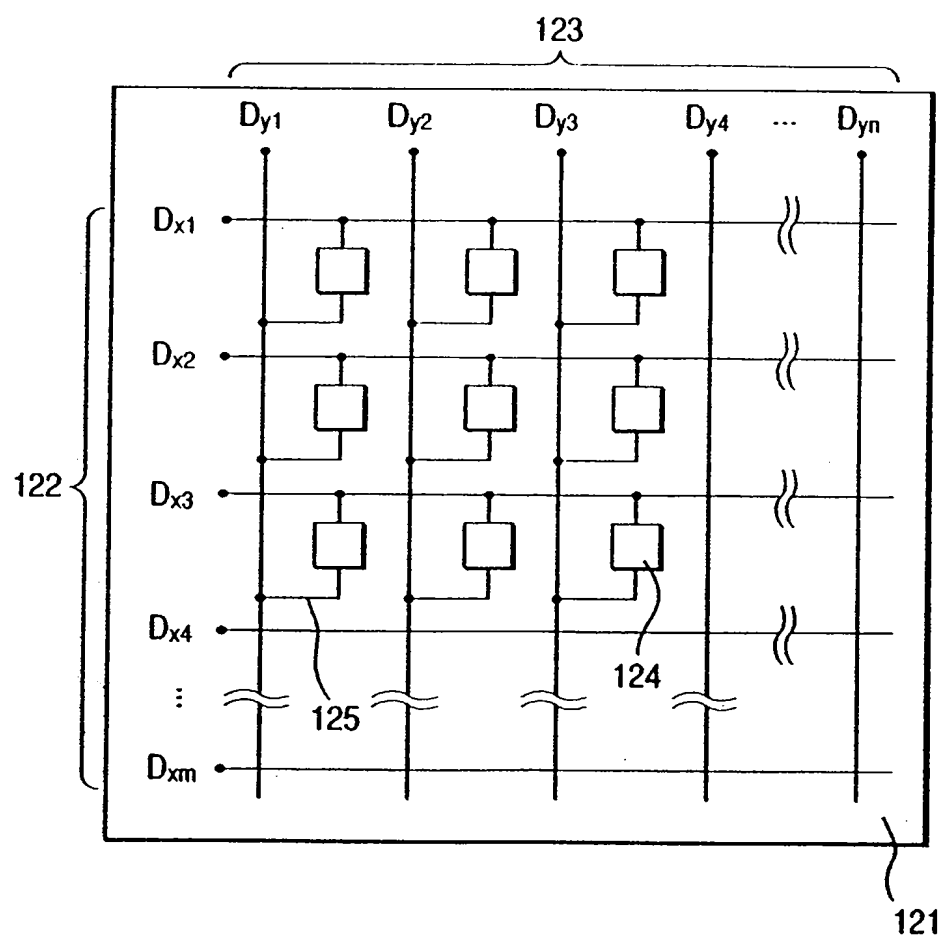


FIG. 13

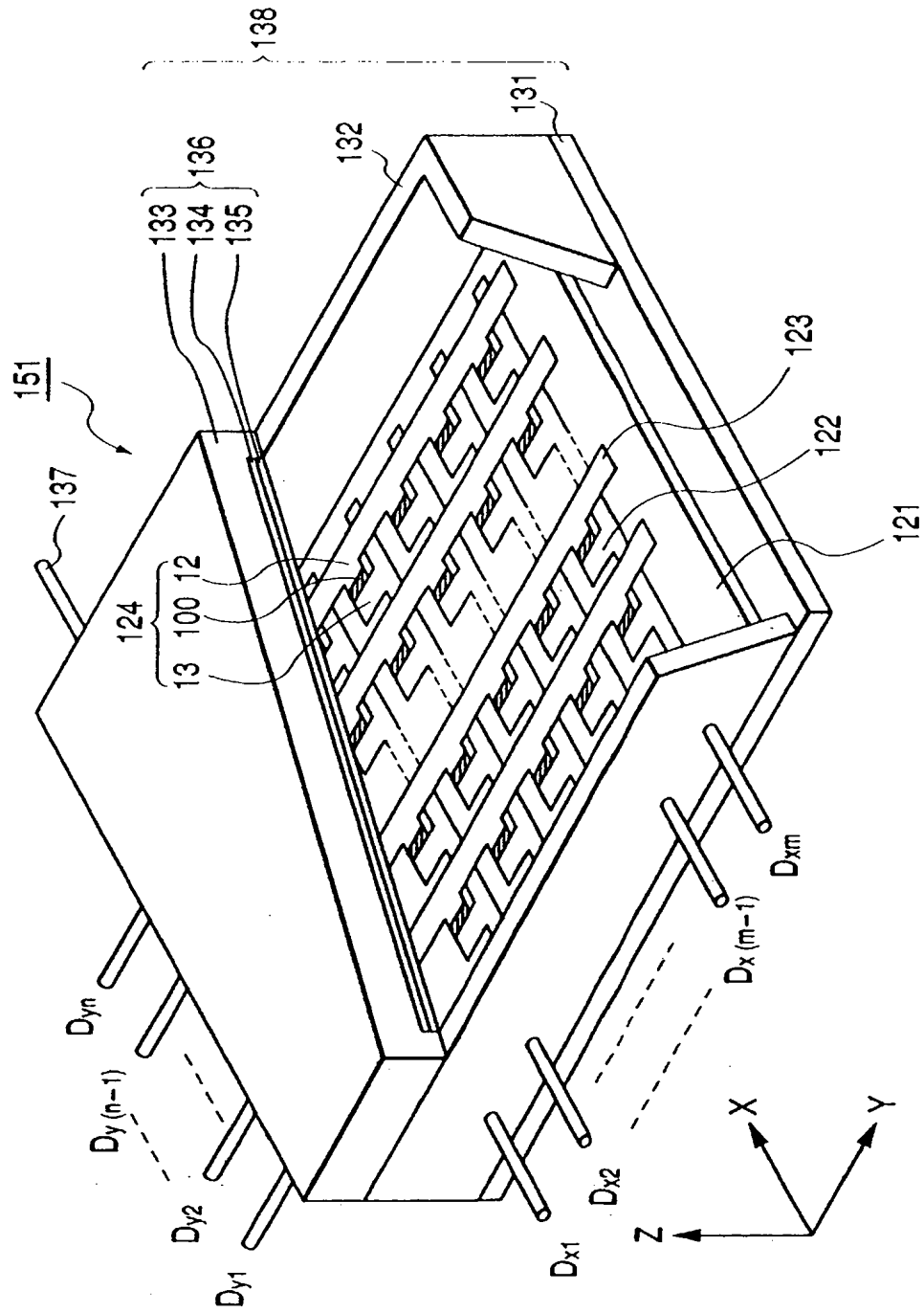


FIG. 14A

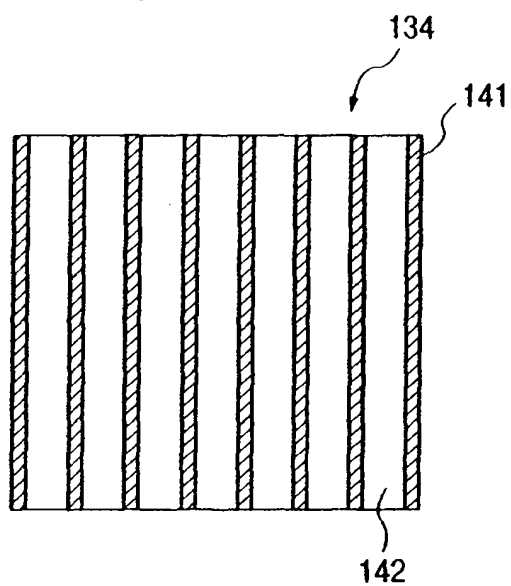


FIG. 14B

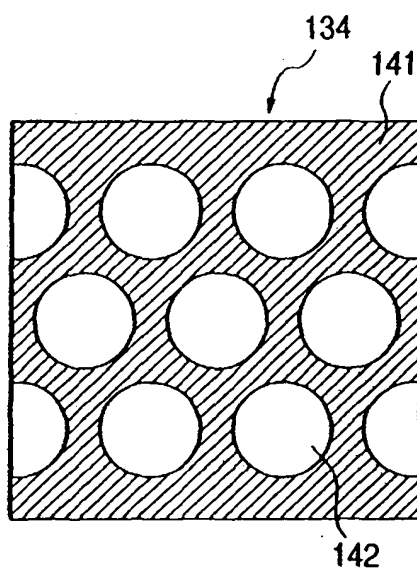


FIG. 15

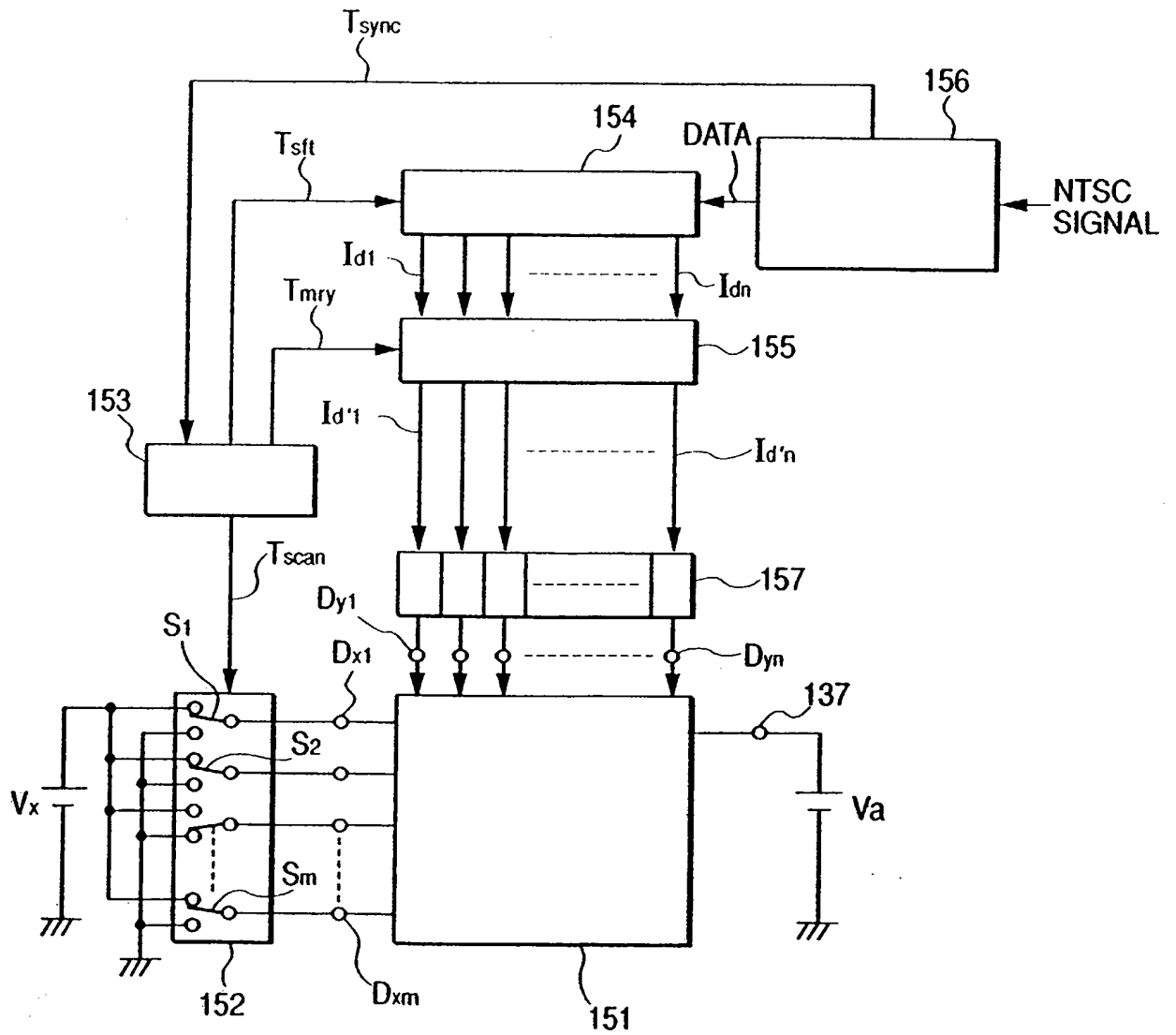
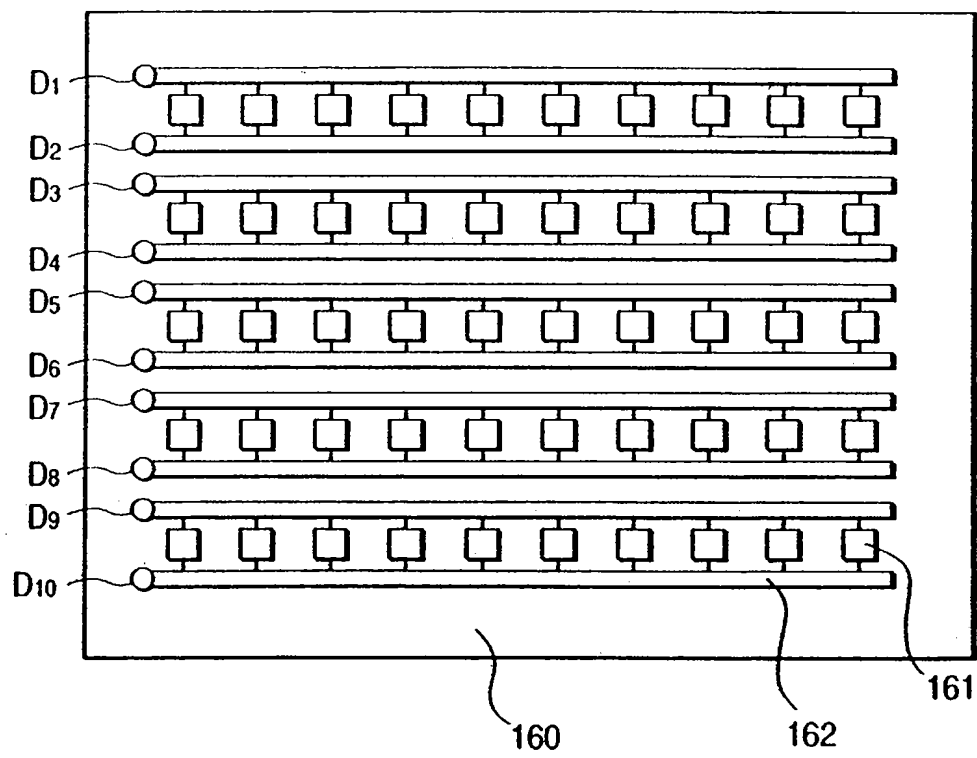


FIG. 16

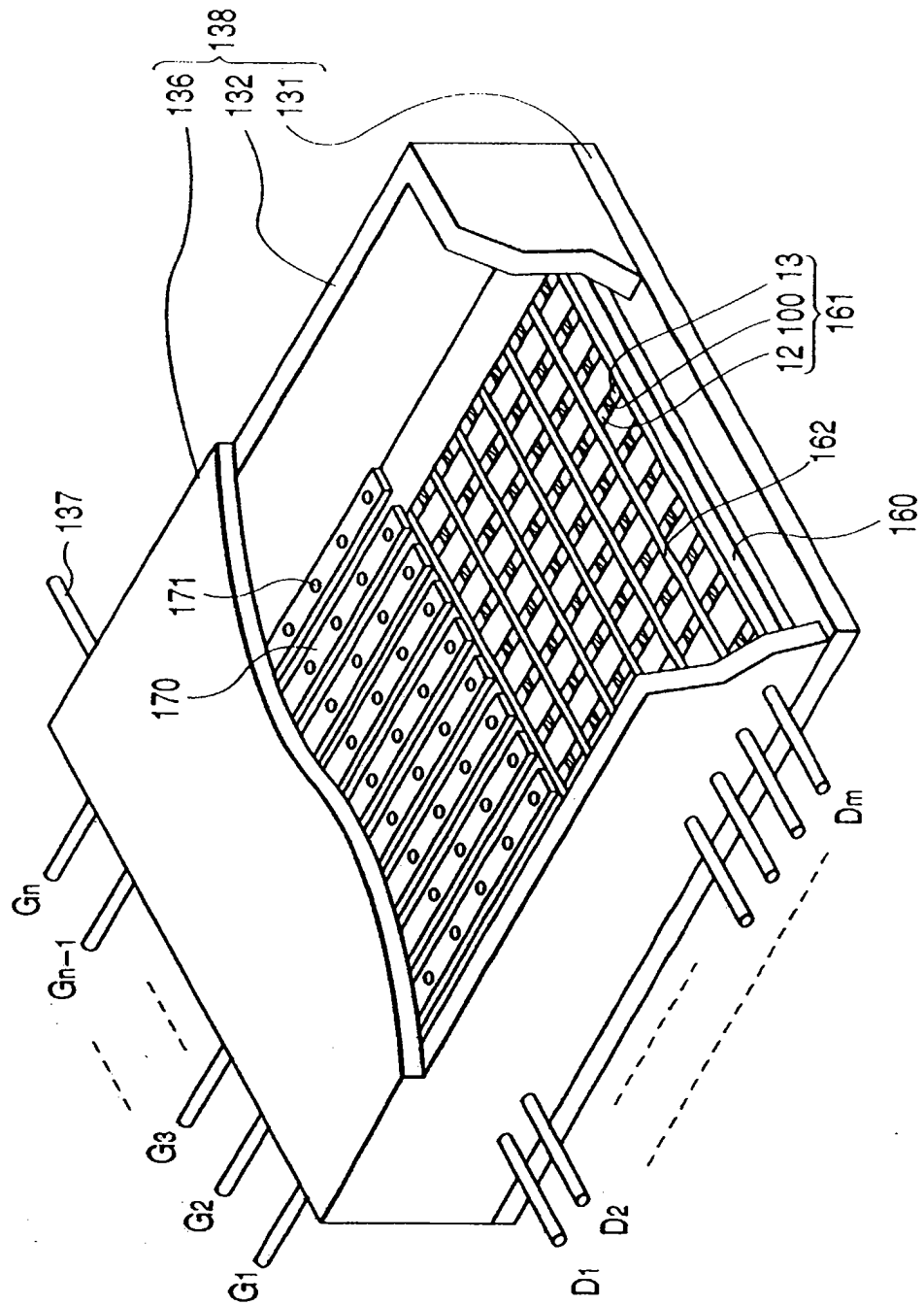


FIG. 18

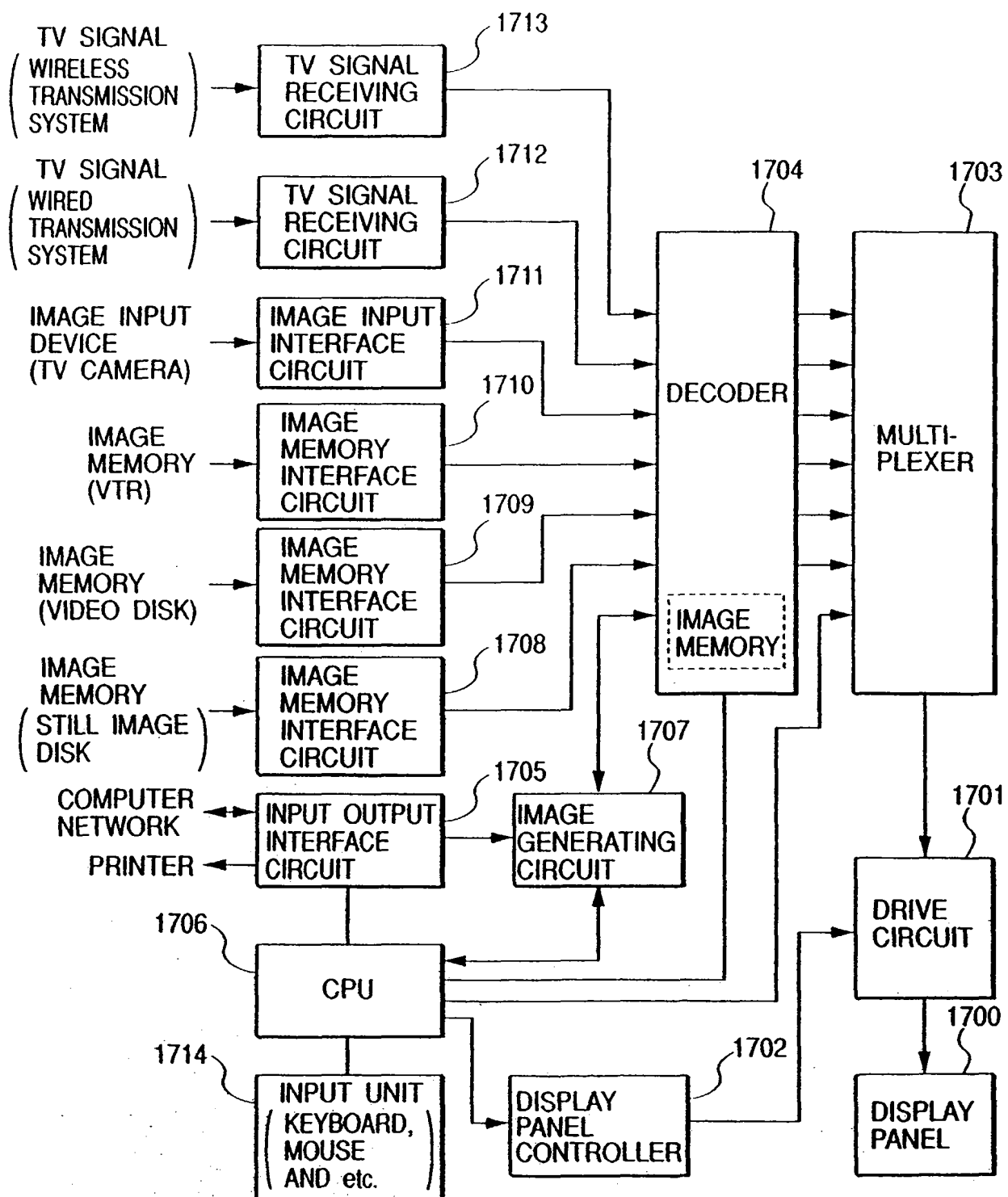


FIG. 19A

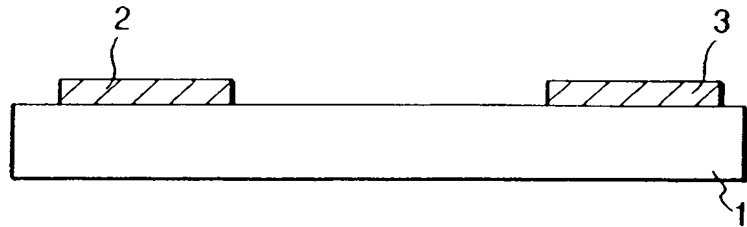


FIG. 19B

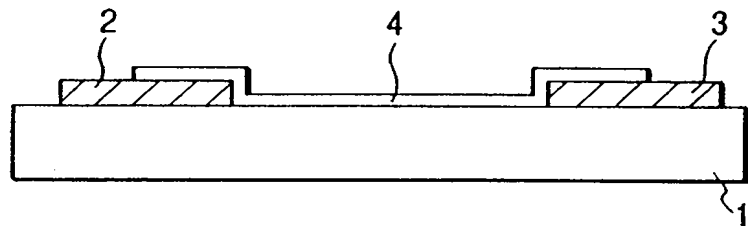


FIG. 19C

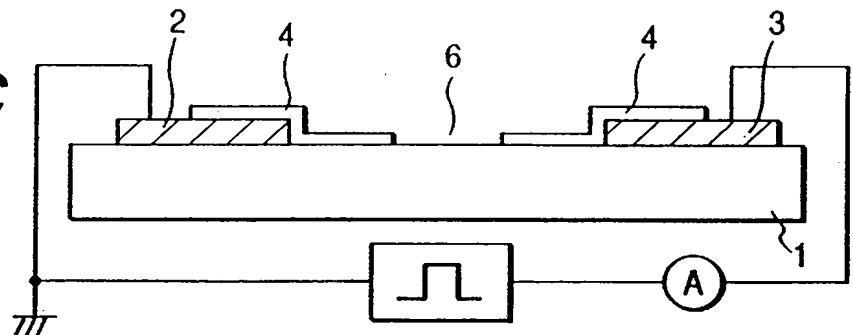


FIG. 19D

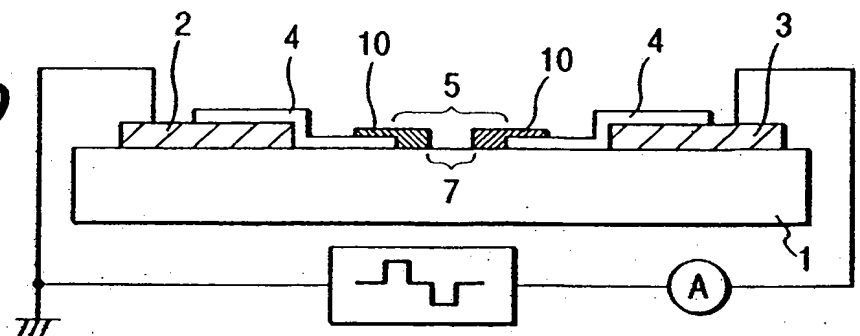


FIG. 20

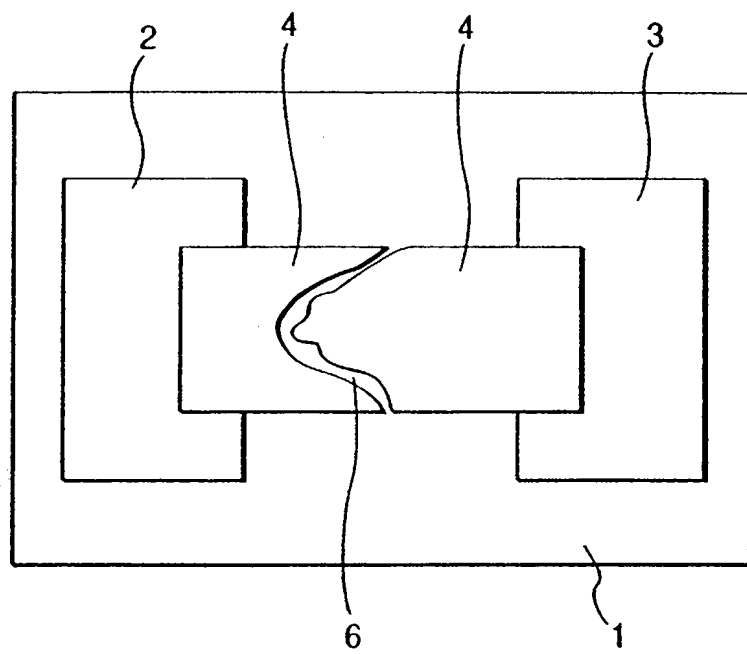


FIG. 21A

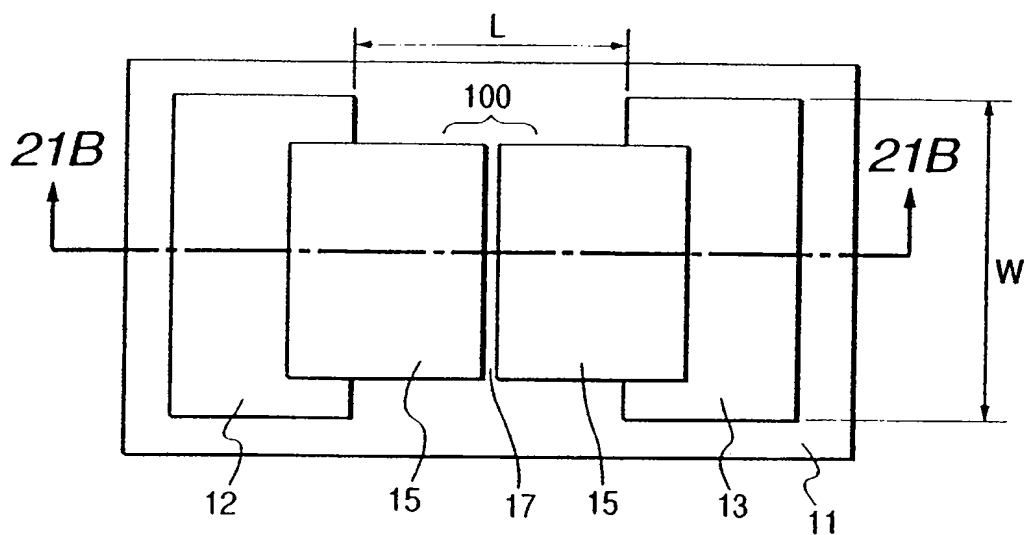


FIG. 21B

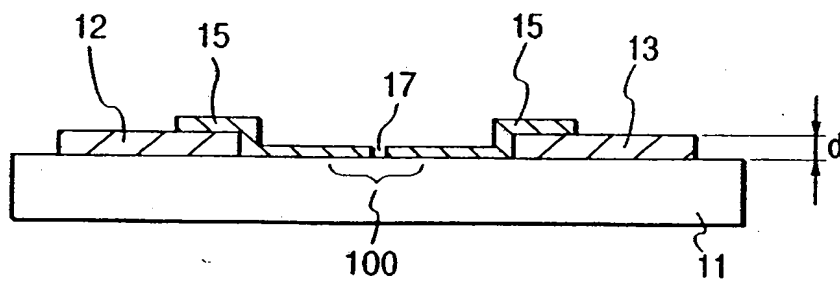


FIG. 22A

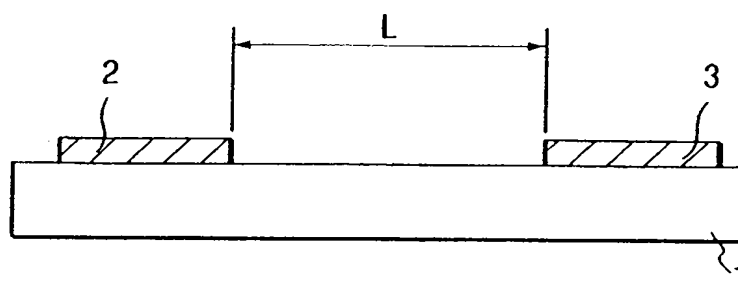


FIG. 22B

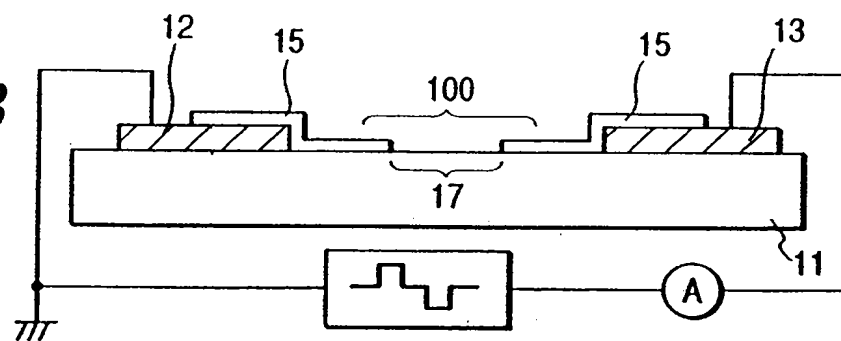


FIG. 23

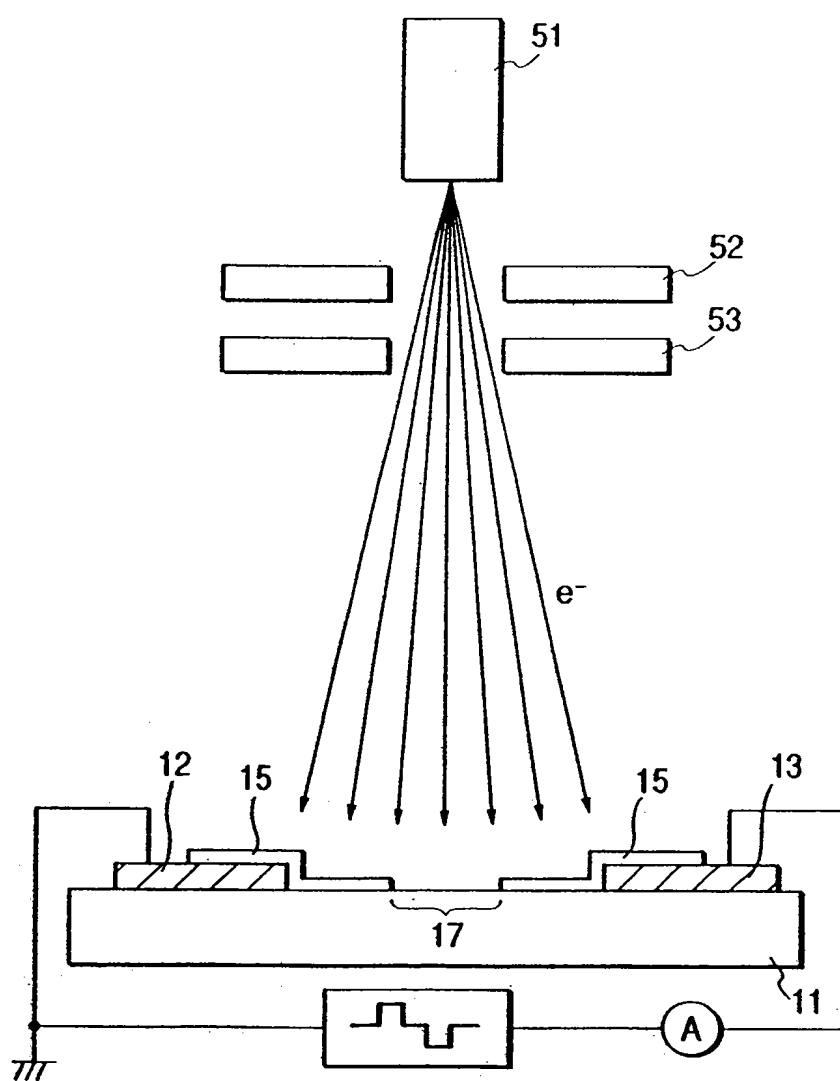


FIG. 24A

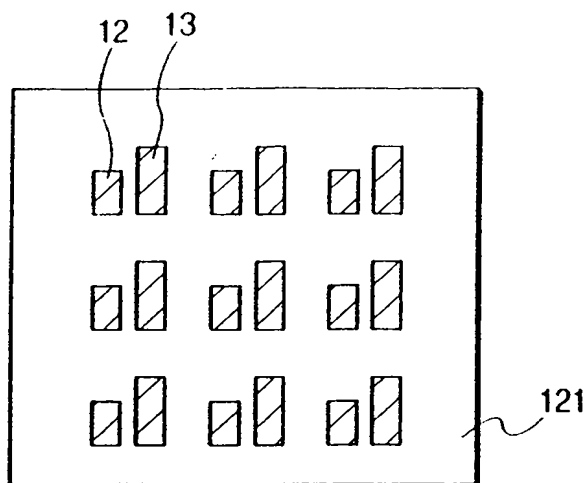


FIG. 24B

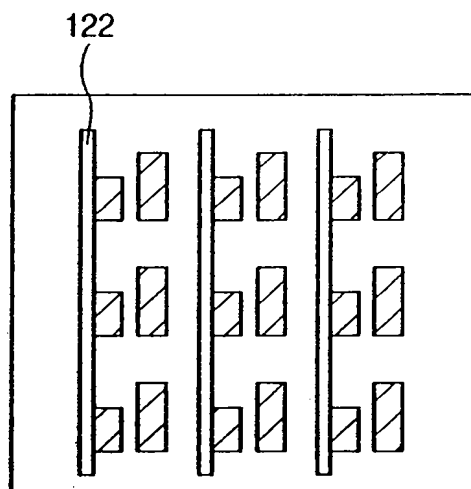


FIG. 24C

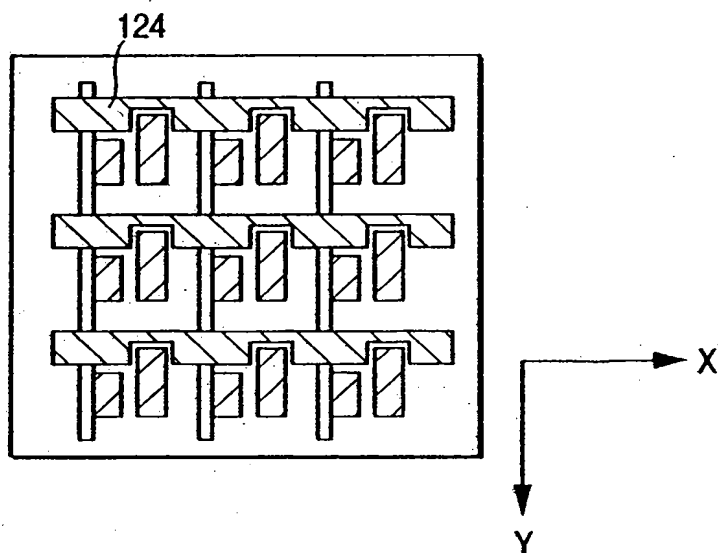


FIG. 25D

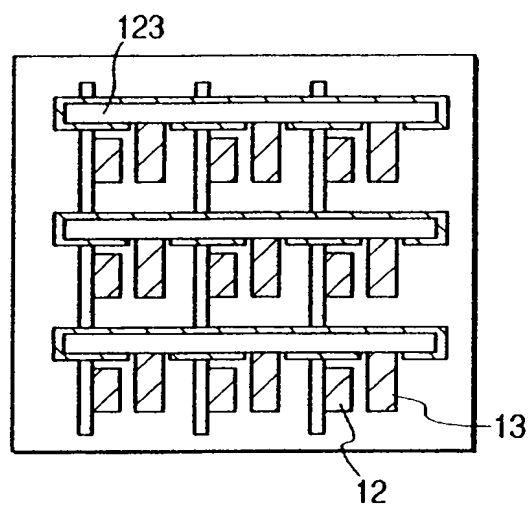


FIG. 25E

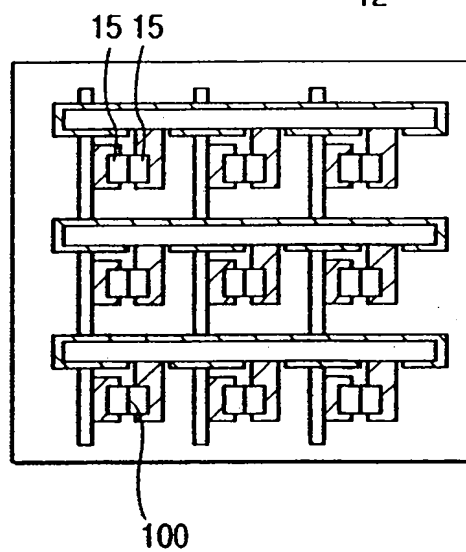


FIG. 26D

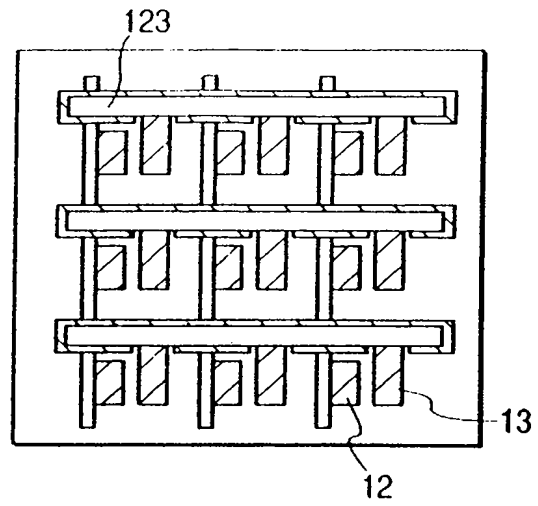


FIG. 26E

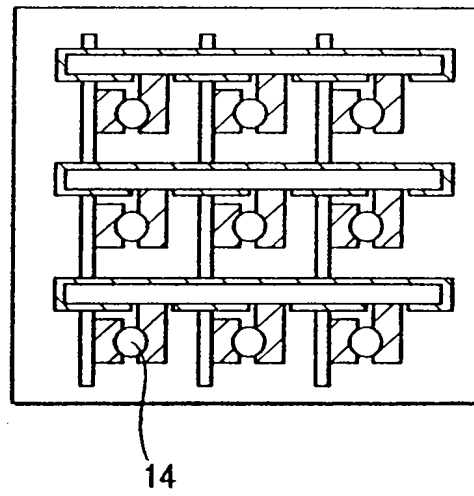
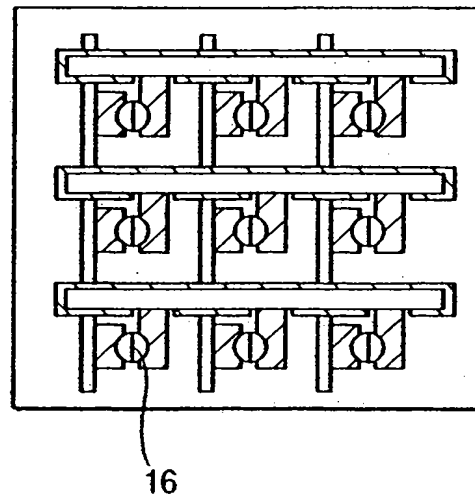


FIG. 26F



- 1 -

TITLE OF THE INVENTION

STRUCTURE HAVING PORES, DEVICE USING THE SAME, AND
/ MANUFACTURING METHODS THEREFOR

BACKGROUND OF THE INVENTIONField of the Invention

10 The present invention relates to minute structures,
devices having minute structures, and manufacturing methods
thereof. In particular, the present invention relates to a
nanoscale structure, a device using the nanoscale structure,
and manufacturing methods thereof. The nanoscale structure
15 of the present invention provided with alumina nanoholes can
be widely used as a functional material and as a structural
material for electronic devices and micro devices. The
present invention can be particularly applied to quantum
effect devices, electrochemical sensors, biosensors,
magnetic memory devices, magnetic devices, light-emitting
20 devices, photonic devices, solar cells, and the like.

Description of the Related Art

Since the movement of electrons is constrained when
thin films, thin wires, and dots of a metal and a
semiconductor are smaller than the distinctive length (such
25 as mean free path or spin scattering length) thereof, they

The attached application:

U.S. Application No.: 09/666,605

Filing Date: 09/28/00

Group Art Unit: 2811

is part of an IDS filed in U.S. Application No.: 09/441,585

may exhibit unique electrical, optical, and chemical characteristics in some cases. From the point of view mentioned above, minute structures (nanostructures) smaller than 100 nanometers (nm), have attracted significant
5 attention as a functional material.

As a method for manufacturing the nanostructure, semiconductor processing techniques, such as fine pattern drawing techniques including photolithography, electron-beam lithography, x-ray lithography, and the like, may be
10 mentioned as examples.

In addition to the method mentioned above, attempts to realize a novel nanostructure using a structure having naturally formed regularity, i.e., a structure which is formed in a self-organizing manner, have been made.
15 Depending on the minute structure used as the base structure, the method mentioned above has the possibility of producing a fine and unique structure superior to that obtained by the conventional method. As a result, much research has been initiated in this area. As an example of a unique structure
20 formed in a self-organizing manner, an anodized alumina film may be considered (refer to R. C. Furneaux et al, "The formation of controlled-porosity membranes from anodically oxidized aluminium" Nature, vol. 337, p. 147 (1989), and the like).

25 When an aluminum (Al) plate is anodized in an acidic

electrolyte, a porous oxide film is formed. Fig. 9 is a schematic cross-sectional view showing a nanostructure having a porous alumina nanohole layer 11 formed on an Al plate 31 by anodization thereof. As shown in Fig. 9, the characteristic of the anodized alumina film is a unique geometric structure thereof, in which extremely fine pores (nanoholes) 12 having diameters $2r$ of a few nm to a few hundreds of nm are disposed at a few tens of nm to a few hundreds of nm intervals $2R$ therebetween. The nanoholes 12 have high aspect ratios. In addition, between the anodized alumina nanoholes 12 and the Al substrate, barrier layers (aluminum oxide layers) 22 exist.

Focusing on the unique geometric structure of alumina nanoholes formed by anodization, various applications thereof have been implemented. Application of anodized films to films using abrasion resistance and insulating properties thereof and application to filters obtained by peeling anodized films are as examples. In addition, by filling the nanoholes with a metal, a semiconductor, or the like or by using a replica of nanoholes (by using nanoholes as a mold), various applications to coloration, a magnetic recording medium, an electroluminescent (EL) light-emitting device, an electrochromic device, an optical device, a solar cell, a gas sensor, and the like have been pursued. Furthermore, applications in various fields have been

anticipated, such as a quantum effect device including a quantum thin wire, a metal insulator metal (MIM) device, a molecular sensor using nanoholes as a chemical reaction field, and the like (see Masuda, "Metal nanohole array having high regularity formed of anodized alumina", KOTAIBUTSURI (Solid State Physics) 31, vol. 31, no. 5, pp. 493-499 (1996), Japanese Patent Laid-Open No. 11-200090).

Concerning the formation of a nanostructure by using semiconductor processing techniques described above, there are problems in that the production yield is low and the apparatuses therefor are costly. Hence, a simple and reproducible manufacturing method has been desired. In view of the points described above, the method using self-organization, in particular, the method of anodizing Al, has advantages in that a nanostructure can be easily and controllably formed.

Since the nanostructure shown in Fig. 9 is only formed on an Al plate surface, the application and the shape thereof are limited to some extent. For example, since the melting point of Al is 660°C, nanoholes formed on the surface thereof cannot be subjected to heating to or above the above-mentioned temperature. Consequently, in order to use nanoholes as a functional material in various fields, a novel technique has been awaited in which an anodized alumina film can be formed on a substrate having a higher

melting point without impairing the unique geometric structure of the anodized alumina or cracking at higher temperatures.

When applications of the minute structure described above to devices are considered, it is important that the pores be filled with a functional material and that a plurality of pores be selectively filled with a functional material.

SUMMARY OF THE INVENTION

Accordingly, it is an object of the present invention to solve the problems described above and to provide a novel and effective minute structure.

One aspect of the present invention is to provide a minute structure in which a plurality of pores having electroconductive paths is selectively disposed above a substrate and to provide a manufacturing method therefor.

Another aspect of the present invention is to provide a minute structure in which a material is selectively filled in some of the plurality of pores disposed above a substrate and to provide a manufacturing method therefor.

Another aspect of the present invention is to provide a nanostructure device using the nanostructure described above.

Another aspect of the present invention is to provide

manufacturing methods for the nanostructure and for the nanostructure device mentioned above.

5 A structure having pores according to the present invention comprises a) a substrate, b) a plurality of electroconductive layers formed on a surface of the substrate, c) a layer primarily composed of aluminum oxide covering the plurality of electroconductive layers and a surface of the substrate where no electroconductive layer is formed, and d) a plurality of pores formed in the layer
10 primarily composed of aluminum oxide, in which the plurality of pores is disposed above the plurality of electroconductive layers and the surface of the substrate where no electroconductive layer is formed, with a part of the layer primarily composed of aluminum oxide provided
15 under the plurality of pores, and in which the layer primarily composed of aluminum oxide, which is provided between the electroconductive layers and the bottoms of pores disposed above the electroconductive layer, comprises a material forming the electroconductive layer.

20 In addition, a method for manufacturing a structure having pores according to the present invention comprises the steps of (A) preparing a substrate, (B) forming a plurality of electroconductive layers each composed of at least one element selected from the group consisting of Ti,
25 Zr, Hf, Nb, Ta, Mo, and W on a part of a surface of the

substrate, (C) forming a film primarily composed of aluminum so as to cover the plurality of electroconductive layers and a surface of the substrate having no electroconductive layer thereon, and (D) anodizing the film primarily composed of
5 aluminum so as to form a layer primarily composed of aluminum oxide having a plurality of pores, in which the plurality of pores is formed above the electroconductive layers and the surface of the substrate having no electroconductive layer thereon, and in which a material
10 forming the electroconductive layer is diffused to a part of the layer primarily composed of aluminum oxide provided between the electroconductive layers and the bottoms of pores above the electroconductive layers.

A device according to the present invention comprises
15 the structure having pores described above.

In addition, an electron-emitting device according to the present invention comprises an electron-emitting material filled in the pores described above.

Furthermore, a magnetic device according to the present
20 invention comprises a magnetic material filled in the pores described above.

A light-emitting device according to the present invention also comprises a light-emitting material filled in the pores described above.

25 Further objects, features, and advantages of the

present invention will become apparent from the following description of the preferred embodiments (with reference to the attached drawings).

5

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A and 1B are schematic views showing a structure of the present invention;

10 Figs. 2A to 2C are schematic cross-sectional views showing manufacturing steps of a structure of the present invention;

Fig. 3 is a schematic view showing an anodization apparatus;

15 Fig. 4 is a graph showing a current profile during anodization in the manufacturing method of a structure of the present invention;

Figs. 5A and 5B are cross-sectional views showing states in anodization in the manufacturing method of a structure of the present invention;

20 Figs. 6A and 6B are cross-sectional views showing states in which electroconductive paths are formed by a diffusion process at the bottoms of pores of a structure of the present invention;

25 Figs. 7A to 7C are cross-sectional views showing states in which a filler is filled in pores of a structure of the

present invention;

Fig. 8 is a schematic view showing an example of a carbon nanotube device of the present invention; and

Fig. 9 is a schematic view showing conventional
5 anodized alumina nanoholes on an Al plate.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Hereinafter, the present invention which solves the problems described above will be described in detail.

10 As an example of the structure of the present invention, a nanoscale structure (a nanostructure) will be described.

The structure of the present invention described herein is a structure comprising a substrate having a first major surface and a second major surface opposing each other and a
15 layer having pores therein disposed on the first major surface. In the structure described above, an electroconductive layer is provided between the layer having pores and the first major surface, electroconductive paths, which electrically connect the electroconductive layer and
20 each bottom edge portion of the pores, are provided in the layer having pores, and the electroconductive layer is patterned so as to be of a desired shape.

Hereinafter, the case in which a substrate in the form of a plate having a first and a second major surface
25 opposing each other, as shown in Fig. 1B, will be described

as an example. However, the present invention will not be limited to the substrate described above, and specifically, any substrate which is suitable for anodization may be used as described below. In the present invention, a substrate
5 having at least one substantially flat surface is preferably used. In addition, a substrate having at least a substantially planar surface is preferably used. That is, the shape of a surface having no layer provided with pores thereon (a second surface in Fig. 1B) is not significant.

10 The nanostructure described above of the present invention will be described in detail with reference to the figures.

Fig. 1A and 1B are schematic views showing the nanostructure of the present invention. Fig. 1A is a plan
15 view of the nanostructure, and Fig. 1B is a cross-sectional view of the nanostructure taken along the line A-A' in Fig. 1A. In Figs. 1A and 1B, numeral 11 indicates a layer having pores 12, numeral 13 indicates a substrate having a first and a second major surface, numeral 14 indicates an
20 electroconductive path, and numeral 15 indicates an electroconductive layer (a metal layer). The first major surface described above is a surface of the substrate provided with the layer 11 having the pores 12.

When the structure described above is formed by
25 anodizing a film (layer) primarily composed of aluminum (Al),

the layer 11 having pores may be called "a layer having pores disposed therein primarily composed of aluminum oxide", "a layer having pores primarily composed of aluminum oxide", or "an alumina nanohole layer" in some cases.

5 When the layer 11 having pores described above is formed by anodization, a film to be anodized is preferably primarily composed of Al. However, another material may be used for a film to be anodized, as long as the material can form pores therein by anodization. In general, formation of
10 the film primarily composed of Al is performed by sputtering or by heat resistance deposition. In addition, there is a method in which an Al foil is used as an Al film, and an electroconductive layer (a metal layer) is formed on one surface thereof. In this case, the thickness of the Al foil
15 is preferably 500 μm or less.

 The electroconductive layer (the metal layer) 15 is preferably composed of Ti, Zr, Hf, Nb, Ta, Mo, W, or the like as a major component. However, a single metal
mentioned above, a mixture thereof, or a mixture with
20 another material may be used. The composition of the electroconductive layer 15 is determined by anodizing conditions, requirements for heat stability, and the like. The formation of the electroconductive layer mentioned above is also generally performed by sputtering or by heat
25 resistance deposition.

The electroconductive layer 15 is patterned so as to be a desired shape. The electroconductive layer 15 optionally has an appropriate form corresponding to a modified embodiment of the structure having pores. For example, the electroconductive layer 15 may be formed of a plurality of electroconductive layers. In addition, the electroconductive layer 15 may be formed so as to have portions thereof (notches or the like) opposing each other with a space therebetween at which the surface of the substrate is exposed.

The inventors of the present invention discovered that ions of a material forming the electroconductive layer 15 migrate to an alumina layer (barrier layer) when anodization of an aluminum portion is completed and oxidation of the electroconductive layer 15 begins, thereby forming the electroconductive paths 14. The electroconductive path 14 tends to be thicker as anodizing time increases. When a metal, a semiconductor, or the like is filled in the pores 12 by electrodeposition, since the electroconductive path 14 works as an electrode, it is preferable that the electroconductive path 14 be thicker to some extent.

When the layer 11 having pores is a layer primarily composed of aluminum oxide (in particular, in the case in which aluminum oxide is obtained by anodizing aluminum), the layer 11 having pores is primarily composed of Al and oxygen

and has a number of columnar pores 12 therein, and the depth directions of the pores (nanoholes) 12 can be disposed approximately perpendicular to the first major surface of the substrate. In addition, individual pores can be
5 disposed substantially parallel to each other and can be disposed at approximately regular intervals therebetween. The term "parallel" indicates that the depth directions of individual pores 12 are substantially parallel to each other.

Furthermore, the pores can be disposed so as to form
10 triangular (honey comb arrangement) as shown in Fig. 1A. The diameter $2r$ of a nanohole is a few nm to a few hundreds of nm, and the interval $2R$ therebetween is approximately a few tens of nm to a few hundreds of nm as shown in Fig. 1B.

When the layer 11 having pores is obtained by anodizing
15 a film primarily composed of aluminum, the thickness of the layer 11 having pores and the depths of the pores thereof can be controlled by the thickness of the film primarily composed of Al before anodizing.

The thickness of the film primarily composed of Al
20 mentioned above is preferably 10 nm to 500 μm . Conventionally, the depths of pores are generally controlled by anodizing time; however, in the present invention, it can be controlled by the thickness of the film primarily composed of Al, so that an alumina nanohole layer having
25 superior uniformity in the depths of pores can be formed.

When a material is selectively filled in desired pores 12 by using electrodeposition, the significance of the effect of patterning of the electroconductive layer 15 can be understood. In addition to electrodeposition, chemical vapor deposition (CVD), electrophoresis, coating, infiltration, or the like may be used.

When a material (a filler) to be filled in pores is a magnetic material, the structure obtained therefrom may be used as a magnetic medium as an effective perpendicular magnetic film, and when the structure is a thin wire of a magnetic or a metallic material, the structure may be used as an effective quantum effect device. In addition, when cobalt (Co) and copper (Cu) are formed alternately in pores as shown in Fig. 7A, a giant magnetoresistive effect (GMR) device having a pattern responding to a magnetic field may be produced.

In addition, when a filler material 23 is a light-emitting material or a fluorescent material, a wavelength-converting layer in addition to a light-emitting device may be formed. Furthermore, when a filler material is a dielectric material other than alumina, an effective photonic device may be formed. In the case mentioned above, a filler material patterned therein is very effective.

Hereinafter, an example of a method for manufacturing the structure of the present invention will be described

with reference to Figs. 2A to 6B. In this case, an example will be described in which a material is filled in pores by electrodeposition.

5 Figs. 2A, 2B, and 2C are schematic views showing manufacturing steps of the structure of the present invention, Fig. 3 is a schematic view showing an anodization apparatus, Fig. 4 is a graph showing a current profile during anodization, and Figs. 5A, 5B, 6A, and 6B are schematic views showing reaction steps of a film 21
10 primarily composed of Al disposed on the electroconductive layer 15 in Fig. 2A.

Manufacturing steps for forming a layer having pores (an alumina nanohole layer) by anodizing an aluminum film will be described.

15 The following steps (a) to (c) correspond to Figs. 2A to 2C, respectively.

(a) Step of Film Formation

A substrate 13 having a first major surface and a second major surface opposing each other is prepared.

20 Next, the electroconductive layer (the metal layer) 15 described above is formed in a desired shape on the first major surface mentioned above.

Subsequently, the film 21 primarily composed of Al (the film to be anodized) is continuously formed on the
25 electroconductive layer 15 and on the first major surface of

the substrate 13 where the electroconductive layer 15 is not formed thereon.

Patterning of the electroconductive layer (the metal layer) 15 of the present invention can be performed by
5 common semiconductor techniques, such as photolithography, metal mask film formation, and the like. Various patterning arrangement may be performed in accordance with applications of a structure having pores.

The following may be considered examples; however, the
10 present invention is not limited thereto.

1) a patterned electroconductive layer (a metal layer) is disposed on an insulating substrate or an insulating layer,

2) a patterned insulating layer is disposed on an
15 electroconductive (a metal) substrate or an electroconductive layer (a metal layer),

3) an electroconductive layer (a metal layer) is formed on a substrate and is then partly insulated, and

4) an insulating layer is formed on a substrate and is
20 partly electrically conductive.

In the case of 1) described above, as the substrate 13, a substrate composed of an insulating material or a film composed of an insulating material provided on a first major surface of an electroconductive substrate may be used.

25 In the case of 2) described above, as the substrate 13,

a substrate composed of an electroconductive material, such as a metal or a semiconductor, or a film composed of an electroconductive material provided on a first major surface of an insulating substrate may be used.

5 In the case of 1) described above, the thickness of the electroconductive layer to be used is preferably 1 nm to 1 μm and more preferably, 5 nm to 0.5 μm , taking account of the anodization electrode and the surface flatness of a layer to be anodized primarily composed of Al.

10 In the case of 2) described above, the thickness of the insulating layer to be used is preferably 1 nm to 1 μm and more preferably, 5 nm to 0.5 μm , in view of the surface flatness of a layer to be anodized primarily composed of Al.

 Depending on the thickness of the film 21 (the film to
15 be anodized) primarily composed of Al, steps (or recesses) reflecting the pattern of the electroconductive layer (or the insulating layer) 15 may be formed on the surface of the film 21 primarily composed of Al. As a result, depending on the depths of the recesses (or the steps), which are
20 approximately equivalent to the thickness of the electroconductive layer (or the insulating layer), and spaces between the adjacent recesses, which are approximately equivalent to the spaces between the adjacent electroconductive layers (or the insulating layers), in the
25 anodizing step described later, anodization (pore formation)

may occur preferentially from the recesses described above. Consequently, pores 12 formed on the electroconductive layer and pores 12 formed on the insulating layer may have shapes different from each other in some cases. Alternatively, the pores may not reach the electroconductive layer 15 in some cases.

On the other hand, in the present invention, in order to uniformly form pores above the electroconductive layer and the insulating layer, the flatness of the film 21 (the film to be anodized) primarily composed of Al must be improved in the case of 1) or 2) above. Accordingly, in the present invention, the thickness of the film 21 primarily composed of Al is set to be not less than 2 times the thickness of the patterned electroconductive layer (or insulating layer) 15, preferably not less than 5 times, and more preferably, not less than 10 times.

By setting the thickness of the film 21 primarily composed of Al and the thickness of the electroconductive layer (or the insulating layer) 15 as described above, pores can be formed without depending on recesses (or steps) formed on the film 21 primarily composed of Al.

In addition, instead of the method described above, the surface of the film 21 primarily composed of Al may be planarized after the formation thereof, and anodization may then be performed. The planarization mentioned above may be

performed by surface polishing, such as chemical etching and electrolytic polishing.

According to the methods described above, in the case 1) or 2) above, pores, which are substantially similar to each other, can be formed above the patterned electroconductive layer (or the insulating layer) and the insulating layer (or the electroconductive layer).

In addition, the film 21 primarily composed of Al and the electroconductive layer 15, which is also called an electrode since it is being used as an electrode during anodization, can be formed by an optional method, such as resistance heating deposition, electron beam (EB) deposition, sputtering, or CVD.

(b) Anodization

Anodization of the film 21 primarily composed of Al is conducted to form the alumina nanohole layer. Anodization can be performed using an anodization apparatus shown in Fig. 3. In Fig. 3, numeral 40 indicates a temperature-controlled bath, numeral 41 indicates a sample, which is typically the substrate 13 provided with the film 21 primarily composed of Al formed in the previous step described above, numeral 42 indicates a cathode formed of a platinum (Pt) plate, numeral 43 indicates an electrolyte, numeral 44 indicates a reaction chamber, numeral 45 indicates a power supply applying an

anodizing voltage, numeral 46 indicates an ampere meter measuring an anodizing current, and numeral 47 indicates a sample holder. In addition to these mentioned above, a computer for automatic control and measurement of a voltage and a current, and the like (not shown in the figure) are provided therewith.

The sample 41 and the cathode 42 are placed in the electrolyte 43 in which the temperature is kept constant by the temperature-controlled bath 40, and anodization is performed by applying a voltage between the sample 41 and the cathode 42 by the power supply 45.

A solution of oxalic acid, phosphoric acid, sulfuric acid, or chromic acid may be used, for example, as the electrolyte 43 used for anodization. Preferably, a solution of sulfuric acid at a low voltage up to approximately 30 V, a solution of phosphoric acid at a high voltage of 80 V or more, and a solution of oxalic acid at a voltage therebetween may be used.

When anodization in an aqueous solution of oxalic acid is performed using the electroconductive layer 15 as an electrode provided with the film 21 primarily composed of Al formed thereon, the current rapidly drops initially, since the surface of the film 21 primarily composed of Al is oxidized (A in Fig. 4 and Fig. 5A). Subsequently, the current gradually increases concomitant with the formation

of pores (nanoholes) and reaches approximately constant value (B in Fig. 4 and Fig. 5B). When the anodization reaches the electroconductive layer 15 and the substrate 13, the current decreases since the oxidation of Al and
5 diffusion of Al ions into an aqueous solution are suppressed (C in Fig. 4).

In this stage, an alumina-insulating layer (a barrier layer 22 in Fig. 2B) is formed at the bottom edge portions of the pores (nanoholes) 12 disposed above the insulating
10 layer (substrate 13). In Fig. 4, the current profile during anodization is indicated by (2) in which the film 21 primarily composed of Al formed on the insulating layer is anodized.

On the other hand, during the anodization, when the
15 electroconductive layer 15 is composed of a material such as Ti, Zr, Hf, Nb, Ta, Mo, or W, and a film 21 primarily composed of Al formed on the electroconductive layer 15 is anodized, the anodizing current gradually decreases after the anodization of Al is complete, as indicated by (1) in
20 Fig. 4. During the decrease in current, electroconductive paths 14 are gradually formed in an alumina layer (an oxide layer) at the bottoms of the pores (nanoholes). The electroconductive paths 14 begin to form at the onset of the decrease in current (Fig. 6A), and subsequently, the
25 electroconductive paths 14 are thicker and the number

thereof increases (Fig. 6B) through anodization.

The "electroconductive path" described above is an area, which is formed by diffusion of a material contained in the electroconductive layer 15 to the alumina layer caused by anodization, composed of an oxide or a hydroxide containing elements of the electroconductive layer 15 and is disposed in the insulating layer (alumina layer) at the bottom of the nanohole 12. When the cross-section of the conductive path 14 is observed by an electron microscope (e.g. transmission electron microscope), the aforementioned area extending from the electroconductive layer 15 to the interior of the nanohole 12 through the insulating layer (alumina layer) at the bottom of the nanohole 12 clearly exists. According to the compositional analysis of this electroconductive path, a significant amount of the element contained in the electroconductive layer 15 is detected.

The electroconductive path is primarily composed of an oxide of the element forming the electroconductive layer 15 and has electric conductivity. In order to further increase conductivity in the electroconductive path, it is preferable that the layer having the pores (the alumina nanohole layer) be annealed in a reducing atmosphere using, for example, hydrogen.

Accordingly, as a major component of the electroconductive layer 15, it is particularly preferable to

use tungsten (W), since W is easily reduced, the coefficient thereof is similar to that of alumina, and the melting point thereof is high among metals. In particular, when the present invention is used as an electron emission source,
5 the characteristics mentioned above are significant. In addition, the oxide of W also has high ion conductivity, so that it can also be used for chemical applications.

In order to sufficiently form the electroconductive paths described above, it is important to stop the
10 anodization when a decrease of 50% or more of constant oxidation current (B in Fig. 4) is observed.

In addition, when the arrangement of pores is regulated, uniformity of the shapes, such as the diameters of pores (nanoholes) and uniformity of electroconductive paths at the
15 bottoms of the pores (nanoholes) are improved. For performing the regulation mentioned above, it is preferable that recesses be formed at appropriate intervals therebetween on the surface of the film 21 primarily composed of Al and that the recesses be used as starting
20 points for forming the pores.

Next, by immersing the structure formed by the manufacturing method described above in an acidic solution, such as a solution of phosphoric acid, the diameters of pores (nanoholes) can be optionally increased. When a
25 concentration of an acid, an immersing time, and a

temperature are properly controlled, a structure provided with pores (nanoholes) having uniform diameters can be obtained.

5 (c) Electrodeposition

In the case in which a metal is selectively electrodeposited in pores formed above the electroconductive layer 15, a layer (alumina nanohole layer) having pores (nanoholes) is immersed in a solution in which a metal to be electrodeposited is present as cations, and a voltage is applied to the electroconductive layer 15. For example, an aqueous solution of cobalt sulfate may be used as the solution mentioned above. In addition, prior to electrodeposition, the electric conductivities of the electroconductive paths 14 are preferably increased by annealing in a reducing atmosphere using hydrogen or the like, since the efficiency of electrodeposition can be improved. As described above, as shown in Fig. 2C, a filler 23 can be selectively disposed in the pores above the electroconductive layer 15.

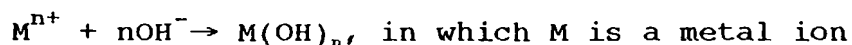
In addition, in order to generate sufficient nuclei during electrodeposition, as a voltage applied to the electroconductive layer 15, an alternating voltage or a pulse voltage is preferably applied.

25 On the other hand, in the case in which anions are

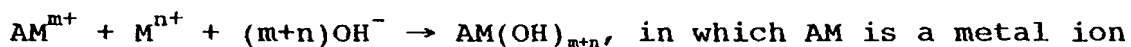
electrodeposited or oxidation is concurrently executed, an application of a positive voltage may be required at some times. In the case mentioned above, an alternating voltage or a pulse voltage is also preferably applied to the electroconductive layer 15.

In the case described above, precipitation of hydroxides by electrolytic oxidation may also occur during electrodeposition. That is, a reaction (I) shown below occurs on the surface of the anode. In addition, when there is another ion, it may be incorporated in the precipitation. That is, a reaction (II) shown below may occur in some cases.

Reaction (I)



Reaction (II)



As shown in Figs. 7B and 7C, according to the present invention, after a desired material (A) is selectively filled in the pores (nanoholes) only disposed above the electroconductive layer 15, another material (B) can be filled in the other pores (nanoholes) by infiltration, CVD, or the like. As described above, different materials can be filled in different pores in accordance with the pattern of

the electroconductive layer 15 as shown in Fig. 7C.

In the case in which the electroconductive layer 15 is composed of a plurality of electroconductive layers, a different material can be filled in pores disposed above a different electroconductive layer. Furthermore, pores filled with a different material can be disposed in each area of the individual electroconductive layers on the same substrate 13.

After filling a desired material in the nanoholes by electrodeposition or the like, it is sometimes effective for the surface of the nanohole layer (a structure having pores) to be planarized so as to be flat.

The alumina nanohole layer obtained from the manufacturing method described above according to the present invention can be applied to various forms, such as a quantum thin wire, a MIM device, a molecular sensor, a coloration application, a magnetic recording medium, an EL light-emitting device, an electrochromic device, an optical device, a solar cell, a gas sensor, an abrasive resistance and insulating film, and a filter.

According to the manufacturing method of the present invention, pores having the electroconductive paths can be selectively disposed only in the desired area on the same substrate.

In addition, according to the manufacturing method of

the present invention, a material, such as a metallic material, can be filled selectively in the pores in a desired area of a structure having a plurality of nanoscale pores. In particular, according to the present invention,
5 by simply patterning the electroconductive layer formed on the substrate, a material, such as a metallic material, can be filled in the desired pores.

As described above, according to the manufacturing method of the present invention, in order to fill only
10 desired pores with a material filled after pore formation, a patterning step for removing or masking unwanted pores is not necessary. When the patterning mentioned above is performed after pore formation, there may actually be serious damage to the nanoscale pores, such as contamination
15 of the pores, breakage of the pores, changes in the shapes of the pores, and the like. Accordingly, since patterning the formed pores is not required in the manufacturing method of the present invention, the method described above is significantly effective.

20 In addition, when an electroconductive layer and a layer primarily composed of Al to be anodized are patterned prior to anodization and are then anodized, an undesirable phenomenon occurs in which the arrangement of pores is disrupted, particularly at portions of patterned edges. As
25 a result, material to be filled in pores is not uniformly

electrodeposited, and a desired structure is difficult to manufacture.

When an x-direction wiring and a y-direction wiring (a matrix wiring) are formed with the layer having pores therebetween, it is preferable that the top and the bottom wirings be formed with a uniform aluminum layer therebetween, so the arrangement of the pores at the edge portions is not disrupted, as described above. In addition, in the case in which a device is produced which is effective when a material is filled in a part of the layer disposed between the top and bottom wirings and is not effective when a material is filled in the entire layer disposed therebetween, a material can be filled in some of the pores by utilizing a part of the bottom wiring as an electroconductive layer, as described above. When the manufacturing method described above is effectively used, a top matrix wiring can be formed in a minute area, even if, for example, an easy selective film formation by using a metal mask is employed. Furthermore, in the case in which matrix driving is performed at a higher speed, the layer in which a material is filled in some of the pores is more advantageous, since the capacitance thereof is smaller than a layer in which a material is filled in all the pores.

According to the structure having pores of the present invention, pores selectively filled with a material

differing from the others can be disposed in each desired area on the same substrate. In addition, when a plurality of electroconductive layers is disposed so as to be electrically isolated from each other, the composition, quantity, and quality of a material to be filled in pores can be altered in each desired area on the same substrate.

As described above, the structure having pores of the present invention is a structure in which pores exist above both electroconductive layer 15 and the insulating layer (an area at which the electroconductive layer is not disposed), "electroconductive paths" are provided at the bottoms of pores disposed above the electroconductive layer 15, and no "electroconductive path" is provided at the bottoms of pores disposed above the insulating layer. Accordingly, when the structure having pores of the present invention is used, a structure can be formed in which, for example, a light-emitting material can be selectively filled by electrodeposition in the pores connected to the electroconductive layer 15 via the electroconductive paths, and no material is filled in the pores other than the pores mentioned above. The structure described above can produce a device in which the intensity of light-emitting wavelengths observed (output) can be altered between the depth direction of the pores and the direction perpendicular thereto.

The reason the device thus described can be produced is believed to be as follows. Since the pores receiving a light-emitting material therein, i.e., a dielectric material, and the pores receiving no material therein are regularly disposed, a two-dimensional photonic device is formed, and a photonic band gap for a specific wavelength is formed in a direction perpendicular to the depth direction of the pores, whereby the light of that wavelength is difficult to transmit.

Hereinafter, referring to the Examples, the present invention will be described.

EXAMPLES

Example 1

In this example, electrodeposition and the shapes of pores when aluminum nanohole layers are formed using various electroconductive layers will be described with reference to Figs. 2A to 2C. Seven samples were made. In each sample, materials used to make the electroconductive films are different from each other.

a) Formation of Electroconductive Layer 15 and Al Film 21

A resist (Hitachi Chemical Co., Ltd., RD-2000N) 1 μm thick was formed by spin-coating on a quartz substrate 13, and a line 10 μm wide was then exposed using a mask and developed. Subsequently, an electroconductive film 100 nm

thick was formed by RF sputtering. As a material for the electroconductive films, Ti, Zr, Hf, Nb, Ta, Mo, and W were respectively used to each sample. The conditions for film formation were set so that the pressure in an Ar atmosphere was 30 mTorr, and the RF power was 500 W. By peeling the resist using a lift-off method, a 10 μm -wide electroconductive layer 15 was formed.

Subsequently, a 1 μm -thick Al film 21 was formed by DC sputtering, whereby a structure shown in Fig. 2A was formed. The conditions for film formation were set so that the pressure in an Ar atmosphere was 20 mTorr, and the DC power was 1,500 W.

b) Anodization

Anodization was performed using an anodization apparatus in Fig. 3.

In this example, an aqueous solution of oxalic acid at a concentration of 0.3 M and an aqueous solution of phosphoric acid at a concentration of 0.3 M were used as an electrolyte, and the electrolyte was maintained at 3°C in a temperature-controlled bath. The anodizing voltage was DC 40 to 100 V, and the electroconductive layer 15 was used as an electrode. During anodization, in order to detect a current indicating the time when anodization of Al, which started from the surface thereof, reached the electroconductive layer 15, an anodizing current was

monitored. The completion of anodization was set to be a point at which a current, after passing the point C shown in Fig. 4, was sufficiently decreased. The time-dependence of an anodizing current during anodization is indicated by (1) in Fig. 4.

After anodization, rinsing using distilled water and isopropyl alcohol was performed, and the diameters of the formed nanoholes were then optionally increased by etching by immersing the sample in a solution of phosphoric acid at a concentration of 5 percent by weight for 45 to 90 minutes.

When the surface and cross-section of the sample obtained were observed by a field emission-scanning electron microscope (an FE-SEM), the Al layer was entirely anodized so as to form aluminum oxide as shown in Fig. 2B, a barrier layer 22 was present at the bottom of the pores (nanoholes) 12 in an area at which an underlayer was the quartz substrate, and on the other hand, electroconductive paths 14 were observed in the barrier layer above the electroconductive layer 15.

In addition, it was confirmed that diameters of the pores (nanoholes) could be controlled by a pore-widening treatment mentioned above.

c) Electrodeposition

Next, Co pillars (a filler) 23 were formed by electrodeposition in nanoholes disposed above the

electroconductive layer 15 of the sample. Cobalt sulfate at a concentration of 5% and boric acid at a concentration of 2% were used as a plating solution, and the AC voltage and the electrodeposition time were respectively set to be 5 V and 30 seconds.

The samples were annealed at 500°C in an H₂ atmosphere for 1 hour prior to electrodeposition, and seven samples for backup were electrodeposited without annealing, which were formed in a manner equivalent to that used for the aforementioned seven samples.

When the cross-sections of the samples were observed by an FE-SEM, the Co pillars were mostly electrodeposited uniformly in the pores above the electroconductive layer 15, and nearly no Co was electrodeposited in the pores above the quartz substrate. Electrodeposition was more uniformly performed in the pores of the annealed sample than in the pores of the sample which was not annealed. The reason for this is believed to be that conductivity of a material forming conductive paths is increased by reduction thereof by heating in an H₂ atmosphere.

It was discovered that selective electrodeposition in the pores 12 can be performed by patterning the electroconductive layer 15.

Next, the surface of the sample electrodeposited with Co was polished using diamond powder, and subsequently, the

sample was disposed so that a magnetic field is parallel to the Co pillars and was then magnetized at 0.8 tesla (T). When the sample was observed by a magnetic force microscope (an MFM), it was confirmed that the Co pillars were
5 uniformly magnetized in the vertical direction (an axial direction of the nanoholes).

Accordingly, it was understood that the present invention could be applied to a magnetic memory and the like.

10 Example 2

In this example, an anodized alumina nanohole layer was formed in a manner similar to that in Example 1.

In this example, a substrate 13 was a quartz substrate, and W was sputtered on the substrate 13 so as to be 100 nm
15 thick and was then patterned by a lift-off method. Anodization was performed in a solution of oxalic acid at a voltage of 40 V at a bath temperature of 10°C and was completed 10 minutes after passing the point C in Fig. 4 at which the anodizing current was sufficiently low. Similarly
20 to Example 1, a pore-widening treatment was performed in a solution of 5 percent by weight of phosphoric acid for 40 minutes.

The sample and a counter electrode made of platinum were immersed in an electrolyte composed of cobalt sulfate
25 at a concentration of 0.5 M and copper sulfate at a

concentration of 0.005 M, and an alternating voltage of 5 V at 50 Hz was applied between the sample and the counter electrode, whereby nuclei of an alloy composed of cobalt and copper were deposited at the bottom of the nanoholes.

5 Subsequently, voltages of -0.5 V and -1.2 V were alternately applied for 20 seconds and 0.1 second, respectively, so that a layered pillar composed of cobalt and copper was grown from the bottom of the nanoholes, whereby a nanostructure shown in Fig. 7A was formed.

10 When a voltage of -0.5 V was applied, only copper that had a lower electrolytic voltage was electrodeposited, and when a voltage of -1.2 V was applied, primarily cobalt, which was at a higher concentration, was electrodeposited, whereby the layered pillar mentioned above could be obtained.

15 Subsequently, a magnetic field dependence of resistance between the electroconductive layer and an electrode mounted at the upper portion of the nanostructure of this example was measured, and a negative magnetic field dependence of resistance was observed.

20 As described above, it was understood that the present invention could be applied to a magnetic sensor having a patterned structure.

Example 3

25 In this example, formation of an alumina nanohole layer

provided with a patterned electroconductive layer 15 composed of Nb formed on a quartz substrate 13 and infiltration of an oxide in pores 12 were performed.

On the quartz substrate 13 provided with the 100 nm-
5 thick patterned electroconductive layer 15 composed of Nb, a 5 μm -thick Al film 21 was formed (Fig. 2A).

Next, recesses arranged in the form of a honeycomb (a hexagonal grating) were formed on the surface of the Al film 21 by lithography. The space between recesses was set to be
10 300 nm.

Subsequently, by performing anodization in a manner similar to that in Example 1, pores 12 (nanoholes) were formed above the substrate 13. In the anodization, a solution of phosphoric acid at a concentration of 0.3 M was
15 used as an electrolyte, the voltage was set to be 140 V, and the completion of anodization was set to be at a time sufficiently long after a decrease in current at the point C in Fig. 4. A pore-widening treatment was then performed for 75 minutes.

20 The sample processed by the pore-widening treatment was immersed in an aqueous solution of zinc nitrate at a concentration of 0.1 M at 60°C together with a counter electrode composed of platinum, and -0.8 V to a reference electrode of Ag/AgCl was applied between the sample and the
25 counter electrode, whereby ZnO crystals were grown in the

nanoholes.

When the surface of the sample was observed by an FE-SEM, the pores 12 were regularly disposed, and it was confirmed that ZnO crystals only grew in the pores above the
5 patterned electroconductive layer 15 composed of Nb, as shown in Fig. 7B.

According to the result of this example, it was understood that ZnO could be filled in specific anodized alumina nanoholes.

10 Since ZnO functions as a light-emitting material and a fluorescent material and is different from adjacent alumina in terms of dielectric constant, it was understood that the present invention could be applied to optical devices.

Photoluminescence was measured by applying ultraviolet
15 light to the ZnO portion. The results were that a broad light emission of 400 to 700 nm centered at 500 nm was detected by photoluminescence observation from the upper portion of the substrate, and a decrease in light-emission, at a longer wavelength from approximately 600 nm, was
20 detected by photoluminescence observation from the lateral direction of the substrate. As described above, when pores receiving no material therein and pores receiving material therein are disposed on a highly regular basis, a device can be obtained in which the intensity of a light-emitting
25 wavelength observed (output) can be altered between the

direction perpendicular to the first major surface of the substrate and the direction parallel thereto.

The reason for this is believed to be that a part of the alumina nanohole layer having regularly disposed pores without ZnO therein functions as a two-dimensional photonic crystal, and hence, a photonic band gap is formed in a longer wavelength region.

Example 4

10 In this example, an alumina nanohole layer was formed by anodization in a manner similar to that in Example 1. In this example, a substrate 13 was a quartz substrate, a film was formed on the substrate 13 by sputtering Nb, and the film was subsequently patterned by a lift-off method so as to form an electroconductive layer 15 shown in Fig. 8.

15 Anodization was performed in a solution of oxalic acid at a concentration of 0.3 M at 40 V. When the electroconductive layer 15 was composed of Nb, since the current monotonically decreased with time as indicated by (1) in Fig. 4,

20 anodization was completed when the current is one-tenth of the current in the region B in Fig. 4 (a constant oxidation current). Subsequently, a pore-widening treatment was performed in a manner similar to that in Example 1.

25 The sample was electrodeposited with cobalt in a plating solution composed of cobalt sulfate at a

concentration of 5% and boric acid at a concentration of 2%, and at an alternating voltage of 5 V for 3 seconds, whereby fine catalytic particles 82 were electrodeposited in nanoholes 12 as shown in Fig. 8.

5 When the cross-section of the electrodeposited sample was observed by an FE-SEM, it was confirmed that electroconductive paths 14 primarily composed of Nb were formed in an alumina-insulating layer above the electroconductive layers 15. In addition, fine cobalt
10 particles (fine catalytic particles 82) were only electrodeposited at the bottoms of the pores (nanoholes) above the electroconductive layers 15. Furthermore, when the sample was annealed at 500°C in an H₂ atmosphere prior to electrodeposition, the uniformity of electrodeposition of
15 cobalt was improved. The reason for this is believed to be that conductivity of the electroconductive paths is improved by annealing in a reducing atmosphere.

Subsequently, by heating the sample in a mixed gas composed of 2% of ethylene (C₂H₄) and 98% of helium (He) at
20 750°C for 1 hour, pillars primarily composed of carbon (carbon nano-tubes) 81 could be grown from the fine catalytic particles 82.

When the sample was observed by an FE-SEM, as shown in Fig. 8, it was confirmed that the carbon nano-tubes were
25 selectively grown from the pores (nanoholes) having the fine

catalytic particles 82 therein. The diameters of the carbon nano-tubes 81 were a few nm to a few tens of nm.

When an anode 83 composed of a fluorescent material is provided in a vacuum apparatus so as to oppose the carbon nano-tubes 81 and to be spaced 1 mm therefrom, and when a
5 voltage of 1 kV was applied to the anode, an electron-emitting current, in addition to fluorescence from the fluorescent material, was observed.

Accordingly, it was confirmed that the carbon nano-tube
10 device of this example could work as a superior electron-emitting material having electron-emitting points at predetermined portions thereof.

According to the results obtained from the examples, it can be confirmed that the present invention has the
15 following advantages.

In order to produce electronic devices and photonic devices, it is significantly effective to perform electrodeposition selectively in nanoholes in desired areas.

As has thus been described, the following advantages
20 can be obtained by the present invention.

When a structure having pores is formed by anodization, by patterning an electroconductive layer composed of a metal containing Ti, Zr, Hf, Nb, Ta, Mo, or W, electroconductive paths can only be formed in the interiors of the nanoholes
25 above the patterned electroconductive layer. In addition,

by using the electroconductive paths thus formed, a material can be filled in the nanoholes in the desired areas.

Accordingly, when the structure according to the present invention is used, a quantum effect device, an

5 electrochemical sensor, an optical device, a magnetic device, a superconducting device, and the like can be realized.

The anodized alumina nanohole layer can be used in various applications, and the range of the applications thereof is significantly broad.

10 The minute structure of the present invention can be used as a functional material by itself, and it can also be used as a basic material and/or a mold for a novel minute structure.

While the present invention has been described with
15 reference to what are presently considered to be the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. On the contrary, the invention is intended to cover various modifications and equivalent arrangements included within
20 the spirit and scope of the appended claims. The scope of the following claims is to be accorded the broadest interpretation so as to encompass all such modifications and equivalent structures and functions.

WHAT IS CLAIMED IS:

1. A structure having pores comprising:

a substrate;

a plurality of electroconductive layers formed on a surface of the substrate;

a layer primarily composed of aluminum oxide covering the plurality of electroconductive layers and the surface of the substrate where no electroconductive layer is formed; and

a plurality of pores formed in the layer primarily composed of aluminum oxide;

wherein the plurality of pores are disposed above the plurality of electroconductive layers and the surface of the substrate where no electroconductive layer is formed, with a part of the layer primarily composed of aluminum oxide provided under the plurality of pores; and

wherein the layer primarily composed of aluminum oxide provided between the bottom of the pores disposed above the electroconductive layer and the electroconductive layer comprises a material forming the electroconductive layer.

2. A structure having pores according to claim 1, wherein the electroconductive layer comprises at least one element selected from the group consisting of Ti, Zr, Hf, Nb,

Ta, Mo, and W.

3. A structure having pores according to either one of claims 1 and 2, wherein the substrate comprises an insulating material.

4. A structure having pores according to either one of claims 1 and 2, wherein the substrate comprises an electroconductive substrate and a film composed of an insulating material provided on a surface of the electroconductive substrate.

5. A structure having pores according to claim 1, further comprising a material different from aluminum oxide filled in at least one of the plurality of pores.

6. A structure comprising pores according to claim 5, wherein the material different from aluminum oxide is filled in at least one pore disposed above the electroconductive layer.

7. A structure having pores according to claim 5, wherein the material filled in at least one pore disposed above the electroconductive layer is different from the material filled in at least one pore above the surface of

the substrate where no electroconductive layer is formed.

8. A structure having pores according to claim 5, wherein the material filled in at least one pore disposed above the electroconductive layer is in electrical contact with the electroconductive layer.

9. A structure having pores according to any one of claims 5 to 8, wherein the material filled in at least one pore disposed above the electroconductive layer is an electroconductive material.

10. A structure having pores according to claim 5, wherein the material is a magnetic material.

11. A structure having pores according to claim 5, wherein the material has a light-emitting function.

12. A structure having pores comprising:
a substrate;
a patterned electroconductive layer formed on a surface of the substrate;

a layer primarily composed of aluminum oxide covering the electroconductive layer and a surface of the substrate surrounding an area at which the electroconductive layer is

provided; and

a plurality of pores formed in the layer primarily composed of aluminum oxide;

wherein the plurality of pores are disposed above the electroconductive layer and the surface of the substrate surrounding the electroconductive layer, with a part of the layer primarily composed of aluminum oxide provided under the plurality of pores; and

wherein the layer primarily composed of aluminum oxide provided between the electroconductive layer and the bottom of the pores disposed above the electroconductive layer comprises a material forming the electroconductive layer.

13. A structure having pores according to claim 12, wherein the electroconductive layer comprises at least one element selected from the group consisting of Ti, Zr, Hf, Nb, Ta, Mo, and W.

14. A structure having pores according to either one of claims 12 and 13, wherein the substrate comprises an insulating material.

15. A structure having pores according to either one of claims 12 and 13, wherein the substrate comprises an electroconductive substrate and a film composed of an

insulating material provided on a surface of the electroconductive substrate.

16. A structure having pores according to claim 12, further comprising a material different from aluminum oxide filled in at least one of the plurality of pores.

17. A structure having pores according to claim 16, wherein the material different from aluminum oxide is filled in at least one pore disposed above the electroconductive layer.

18. A structure having pores according to claim 16, wherein the material filled in at least one pore disposed above the electroconductive layer is different from the material filled in at least one pore above the surface of the substrate surrounding an area at which the electroconductive layer is provided.

19. A structure having pores according to any one of claims 16 to 18, wherein the material filled in at least one pore disposed above the electroconductive layer is in electrical contact with the electroconductive layer.

20. A structure having pores according to any one of

claims 16 to 18, wherein the material filled in at least one pore disposed above the electroconductive layer is an electroconductive material.

21. A structure having pores according to claim 16, wherein the material is a magnetic material.

22. A structure having pores according to claim 16, wherein the material has a light-emitting function.

23. An electron-emitting device comprising an electron-emitting material provided in at least one pore of a structure having pores according to either one of claims 1 and 12.

24. A magnetic device comprising a magnetic material provided in at least one pore of a structure having pores according to either one of claims 1 and 12.

25. A light-emitting device comprising a light-emitting material provided in at least one pore of a structure having pores according to either one of claims 1 and 12.

26. A method for manufacturing a structure having

pores comprising the steps of:

preparing a substrate;

forming a plurality of electroconductive layers each composed of at least one element selected from the group consisting of Ti, Zr, Hf, Nb, Ta, Mo, and W on a part of a surface of the substrate;

forming a film primarily composed of aluminum so as to cover the plurality of electroconductive layers and a surface of the substrate having no electroconductive layer thereon; and

anodizing the film primarily composed of aluminum so as to form a layer primarily composed of aluminum oxide having a plurality of pores;

wherein the plurality of pores is formed above the electroconductive layer and the surface of the substrate having no electroconductive layer thereon, and

wherein a material forming the electroconductive layer is diffused to a part of the layer primarily composed of aluminum oxide provided between the electroconductive layer and the bottom of the pores above the electroconductive layer.

27. A method for manufacturing a structure having pores according to claim 26, wherein the substrate comprises an insulating material.

28. A method for manufacturing a structure having pores according to claim 26, wherein the substrate comprises an electroconductive substrate and a film composed of an insulating material provided on the electroconductive substrate.

29. A method for manufacturing a structure having pores according to claim 26, wherein the electroconductive layer is an electroconductive film formed on the surface of the substrate, and the film primarily composed of aluminum is formed so that the thickness thereof is not less than two times the thickness of the electroconductive layer.

30. A method for manufacturing a structure having pores according to claim 26, wherein the electroconductive layer is an electroconductive film formed on the surface of the substrate, and the film primarily composed of aluminum is formed so that the thickness thereof is not less than five times the thickness of the electroconductive layer.

31. A method for manufacturing a structure having pores according to claim 26, wherein the electroconductive layer is an electroconductive film formed on the surface of the substrate, and the film primarily composed of aluminum

is formed so that the thickness thereof is not less than ten times the thickness of the electroconductive layer.

32. A method for manufacturing a structure having pores according to claim 26, further comprising a step of increasing the diameter of the pores by etching after the anodizing step.

33. A method for manufacturing a structure having pores according to claim 26, further comprising a step, prior to the anodizing step, of forming a recess on a surface of the film primarily composed of aluminum disposed so as to cover the plurality of electroconductive layers and the surface of the substrate having no electroconductive layer thereon.

34. A method for manufacturing a structure having pores according to claim 26, further comprising a step of depositing a material selectively in at least one pore disposed above the electroconductive layer by applying a voltage thereto in a solution, wherein the material deposited in the pore by electrodeposition is ionized in the solution.

35. A method for manufacturing a structure having

pores according to claim 34, wherein the voltage applied to the electroconductive layer is an alternating voltage or a pulse voltage.

36. A method for manufacturing a structure having pores comprising the steps of:

preparing a substrate;

forming a patterned electroconductive layer composed of at least one element selected from the group consisting of Ti, Zr, Hf, Nb, Ta, Mo, and W on a part of a surface of the substrate;

forming a film primarily composed of aluminum so as to cover the electroconductive layer and a surface of the substrate having no electroconductive layer thereon; and

anodizing the film primarily composed of aluminum so as to form a layer primarily composed of aluminum oxide having a plurality of pores;

wherein the plurality of pores is formed above the electroconductive layer and the surface of the substrate having no electroconductive layer thereon, and

wherein a material forming the electroconductive layer is diffused to a part of the layer primarily composed of aluminum oxide provided between the electroconductive layer and the bottom of the pores above the electroconductive layer.

37. A method for manufacturing a structure having pores according to claim 36, wherein the substrate comprises an insulating material.

38. A method for manufacturing a structure having pores according to claim 36, wherein the substrate comprises an electroconductive substrate and a film composed of an insulating material provided on the electroconductive substrate.

39. A method for manufacturing a structure having pores according to claim 36, wherein the electroconductive layer is an electroconductive film formed on the surface of the substrate, and the film primarily composed of aluminum is formed so that the thickness thereof is not less than two times the thickness of the electroconductive layer.

40. A method for manufacturing a structure having pores according to claim 36, wherein the electroconductive layer is an electroconductive film formed on the surface of the substrate, and the film primarily composed of aluminum is formed so that the thickness thereof is not less than five times the thickness of the electroconductive layer.

41. A method for manufacturing a structure having pores according to claim 36, wherein the electroconductive layer is an electroconductive film formed on the surface of the substrate, and the film primarily composed of aluminum is formed so that the thickness thereof is not less than ten times the thickness of the electroconductive layer.

42. A method for manufacturing a structure having pores according to claim 36, further comprising a step of increasing the diameter of the pores by etching after the anodizing step.

43. A method for manufacturing a structure having pores according to claim 36, further comprising a step, prior to the anodizing step, of forming a recess on a surface of the film primarily composed of aluminum disposed so as to cover the electroconductive layer and the surface of the substrate having no electroconductive layer thereon.

44. A method for manufacturing a structure having pores according to claim 36, further comprising a step of depositing a material selectively in at least one pore disposed above the electroconductive layer by applying a voltage thereto in a solution, wherein the material deposited in the pore by electrodeposition is ionized in the

solution.

45. A method for manufacturing a structure having pores according to claim 44, wherein the voltage applied to the electroconductive layer is an alternating voltage or a pulse voltage.

ABSTRACT OF THE DISCLOSURE

A minute structure is provided in which electroconductive paths are only formed in nanoholes, and a material is filled in the nanoholes, which are disposed in a specific area, by using the electroconductive paths. The minute structure comprising pores comprises a) a substrate, b) a plurality of electroconductive layers formed on a surface of the substrate, c) a layer primarily composed of aluminum oxide covering the plurality of electroconductive layers and a surface of the substrate where no electroconductive layer is formed, and d) a plurality of pores formed in the layer primarily composed of aluminum oxide, in which the pores are disposed above the electroconductive layers and the surface of the substrate where no electroconductive layers is formed, with a part of the layer primarily composed of aluminum oxide provided under the bottoms of the pores, and in which the layer primarily composed of aluminum oxide provided between the electroconductive layer and the bottoms of the pores disposed above the electroconductive layer comprises a material forming the electroconductive layer.

FIG. 1A

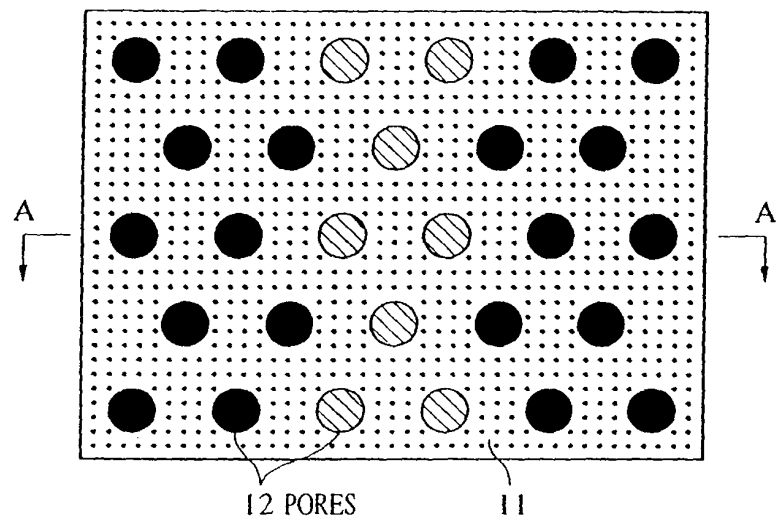


FIG. 1B

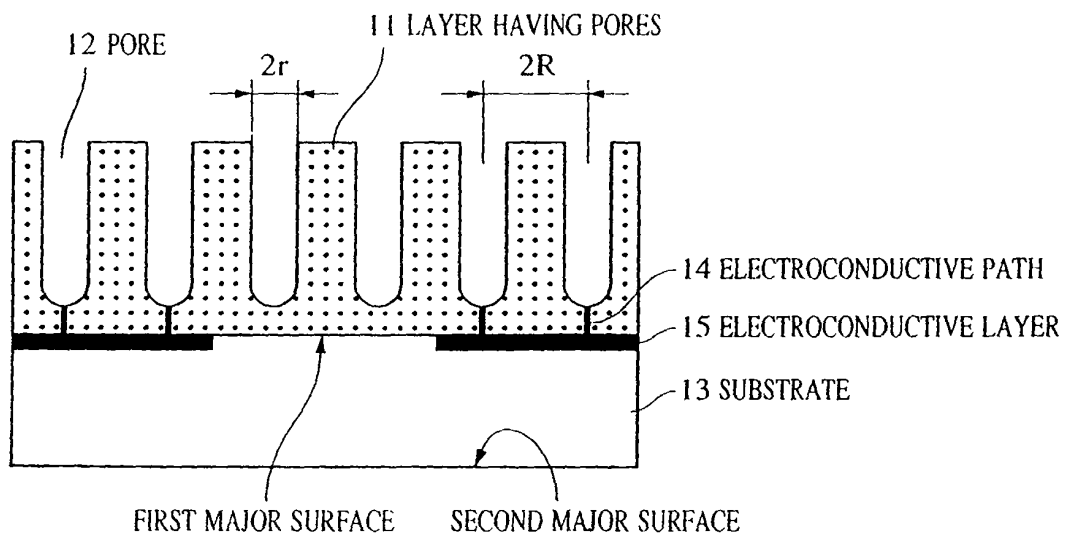


FIG. 2A

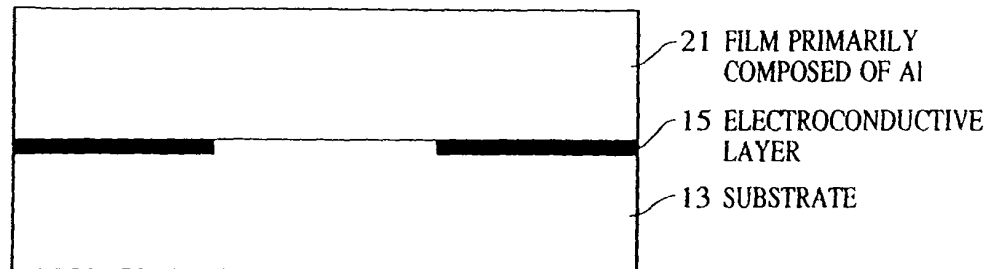


FIG. 2B

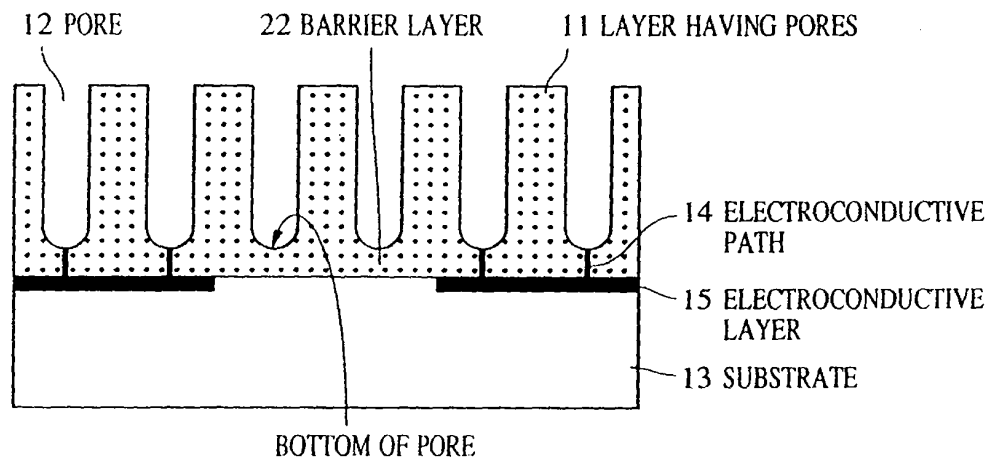


FIG. 2C

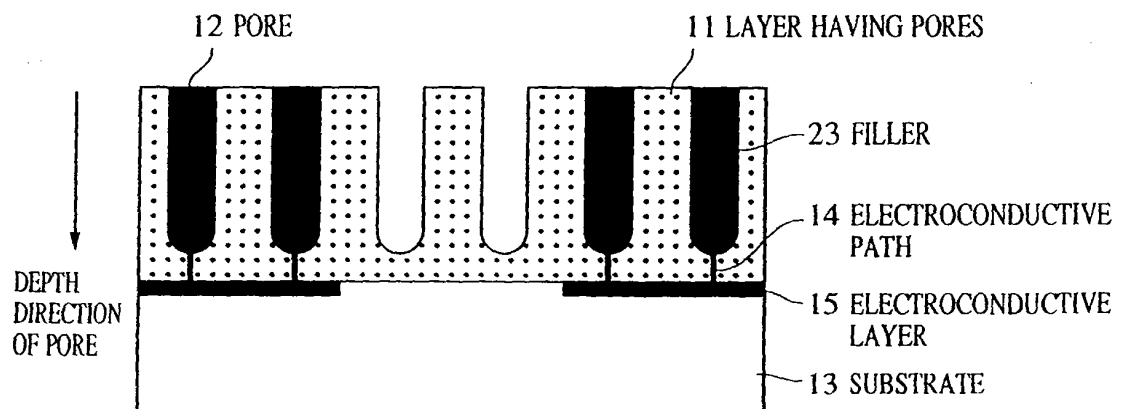


FIG. 3

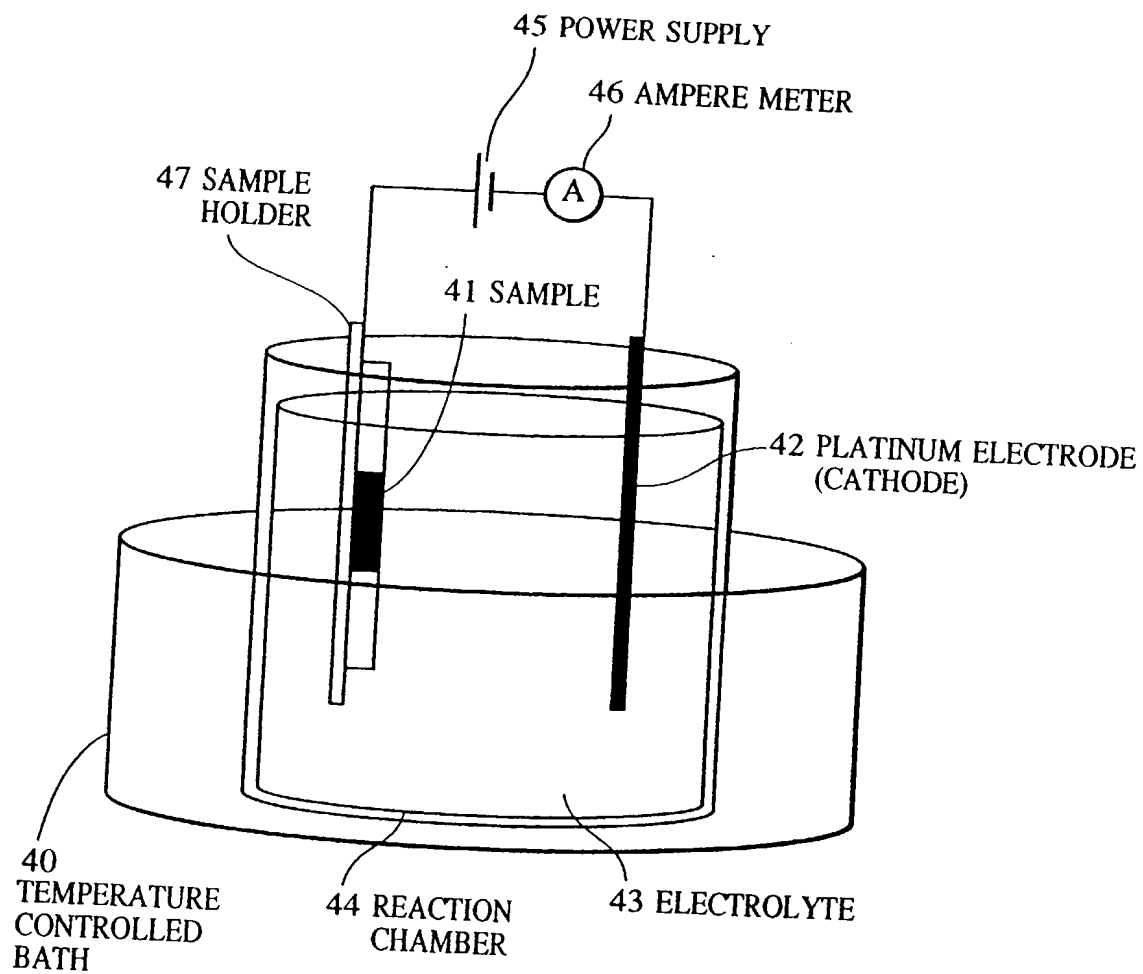


FIG. 4

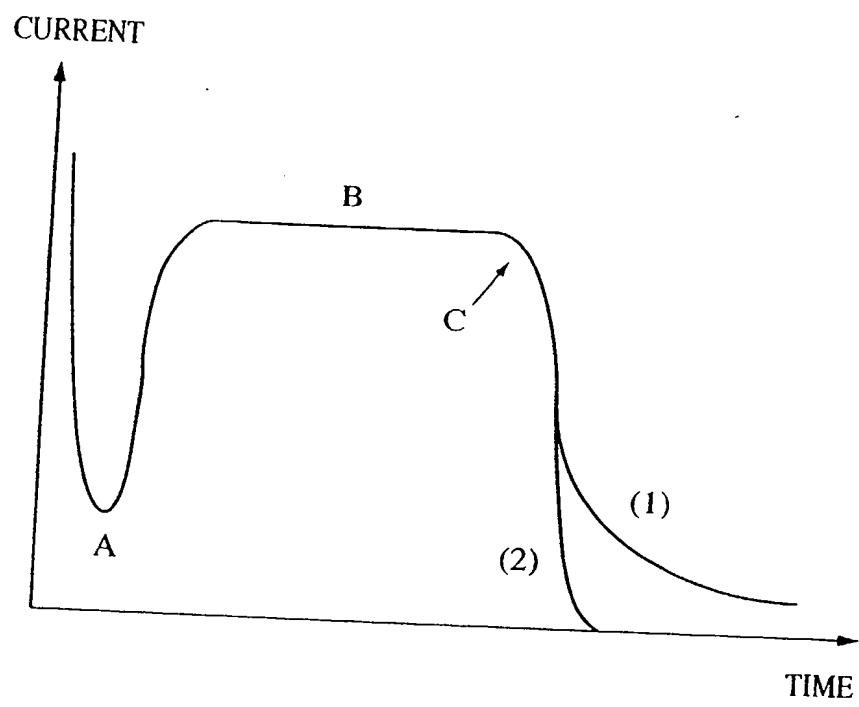


FIG. 5A

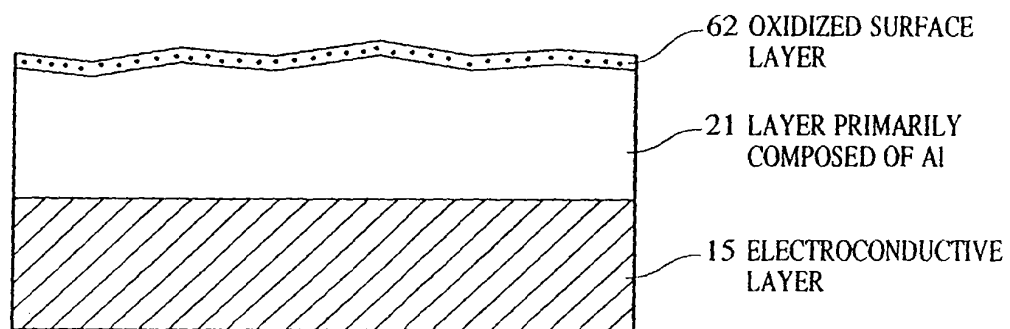


FIG. 5B

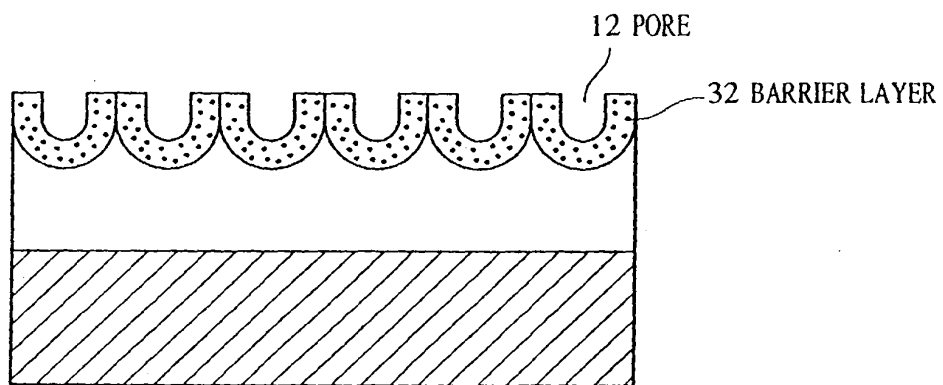


FIG. 6A

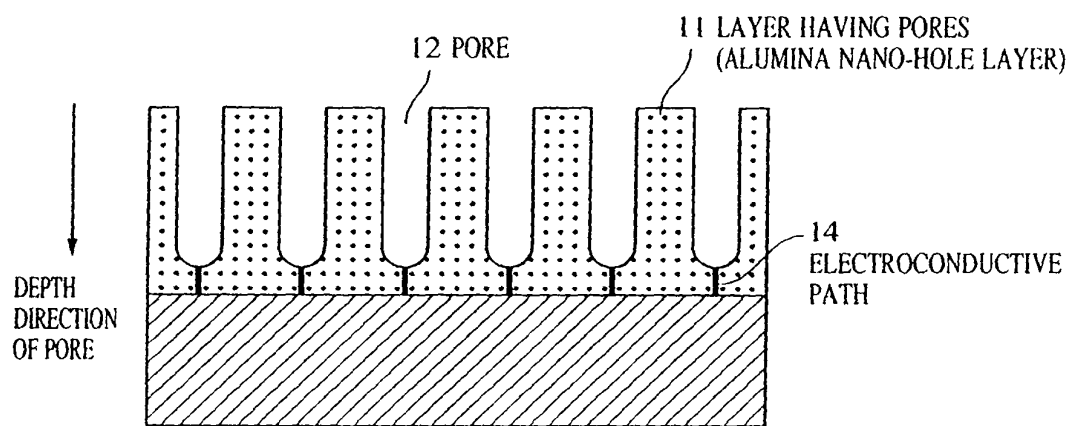


FIG. 6B

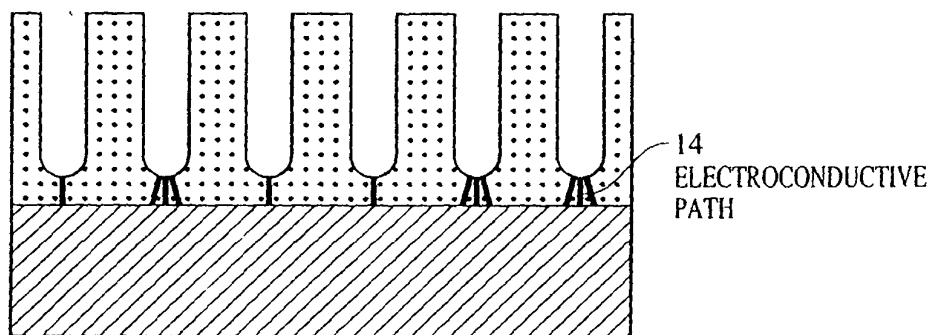


FIG. 7A

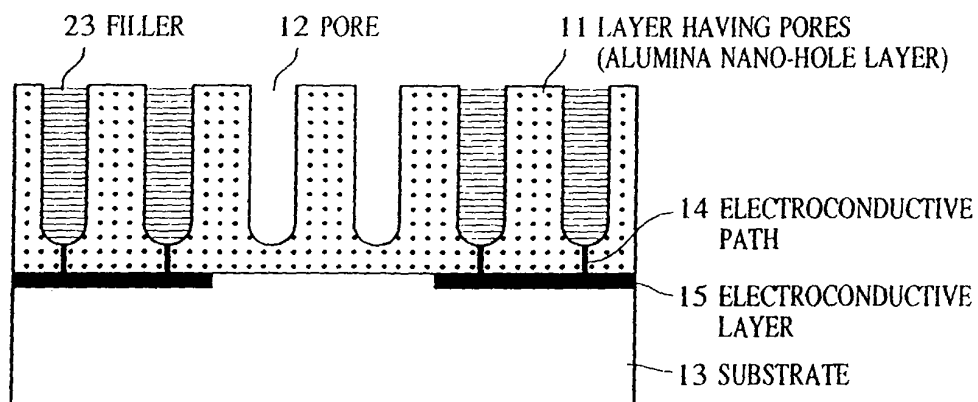


FIG. 7B

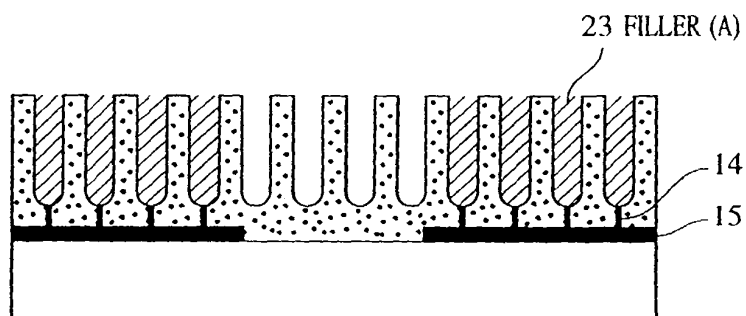


FIG. 7C

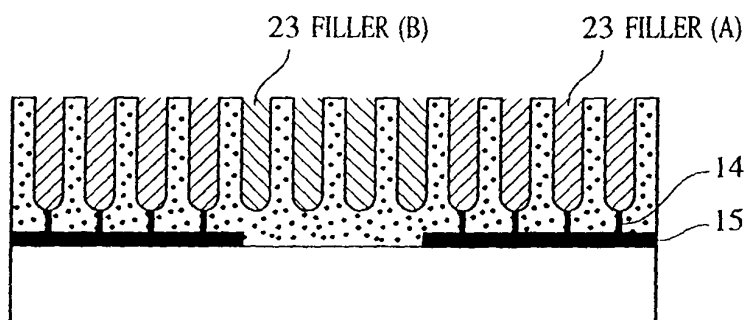


FIG. 8

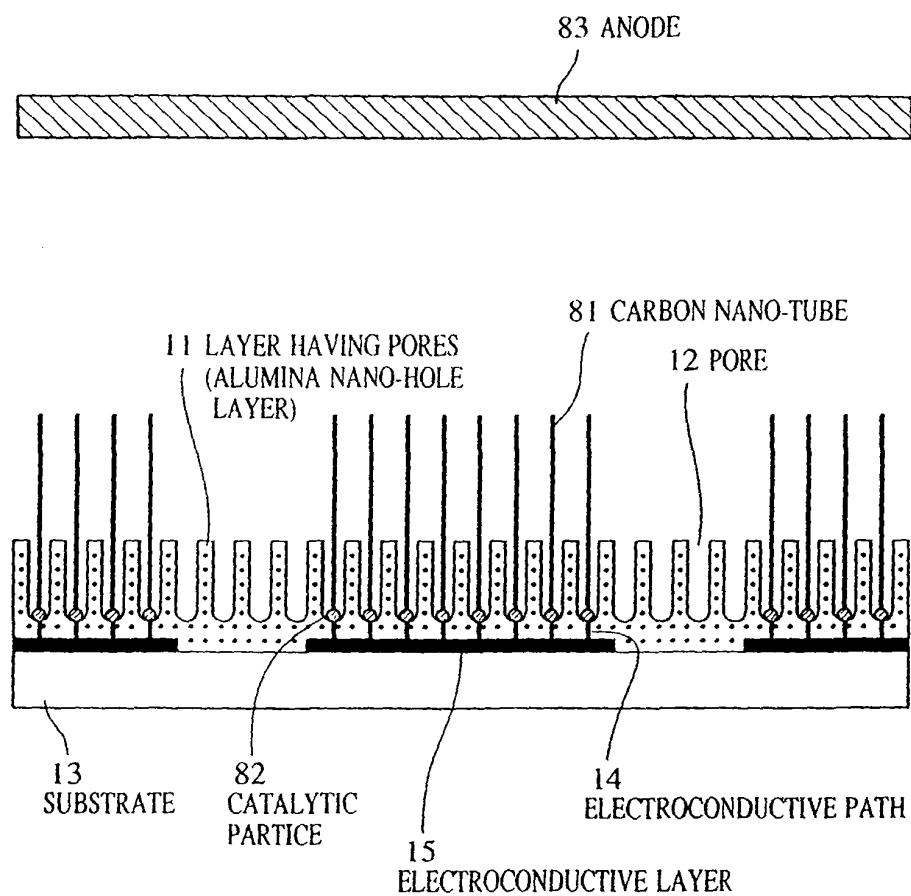
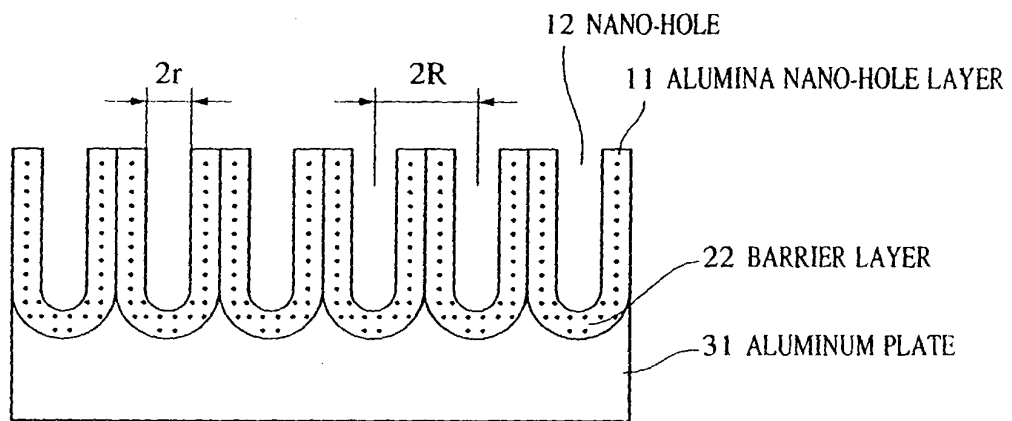


FIG. 9



PRIOR ART

The attached application:
U.S. Application No.: 09/955,137
Filing Date: 09/19/01
Group Art Unit: 2879

is part of an IDS filed in U.S. Application No.: 09/941,515

- 1 -

CFO 15 09 US
09/955,137
D/F - 9-19-01

ELECTRON-EMITTING DEVICE, ELECTRON SOURCE, GAU 2879
IMAGE FORMING APPARATUS,
AND
ELECTRON-EMITTING APPARATUS

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an electron-emitting device, an electron-emitting apparatus using
10 the electron-emitting device, an electron source in which a plurality of the electron-emitting devices are arranged, and an image-forming apparatus constructed using the electron source.

Related Background Art

15 There have been conventionally known two types of electron-emitting devices: thermionic cathode electron-emitting devices and cold cathode electron-emitting devices. The cold cathode electron-emitting devices include, in the category thereof, devices of electric
20 field emitting type (hereinafter referred to as the "FE" type), devices of metal/insulating layer/metal type (hereinafter referred to as the "MIM" type), and surface conduction electron-emitting devices. The FE type electron-emitting devices include devices of diode
25 type that extract electrons using anode electrodes and devices of edge emitter type that emit electrons from edge portions of emitters.

As the diode type electron-emitting devices, there has been known an device disclosed in US Patent No. 5551903.

5 As the edge emitter type electron-emitting devices, there have been known devices disclosed in Japanese Patent Application Laid-open No. 10-289650 and Japanese Patent Application Laid-open No. 8-298068.

SUMMARY OF THE INVENTION

10 In the case of the conventional techniques described above, there occur the following problems.

The application of electron-emitting devices to image-forming apparatuses, such as displays, needs enough emission current to have phosphor emit light
15 having sufficient brightness. Also, to achieve high-definition displays, it is necessary that the diameter of electron beam applied onto phosphor are small and electron-emitting characteristics are uniform. Further, it is important that the electron-emitting
20 devices are driven at low voltage and are easy to be manufactured.

Fig. 16 shows an example of the foregoing diode type electron-emitting devices among the FE-type electron-emitting devices.

25 The electron-emitting device in this example has a construction where a conductive material 302 is disposed on a substrate 301, a convex portion 304 made

of a conductive material is formed on the conductive material 302, an electron-emitting film 305 is laminated on the top end of the convex portion 304, and electrons are extracted by an anode 306 disposed above these components. With this construction, however, the maximum electric field is applied to the end portion of the electron-emitting film 305, so that the beam diameter of emitted electrons tends to be increased.

Also, because electrons are extracted by the voltage applied to the anode 306, a large anode voltage is required in order to have a phosphor (not shown) arranged at the back of the anode 306 emit light having sufficient brightness. However, because the anode 306 doubles as a modulation voltage in this construction, it is difficult to apply a high voltage to the anode 306.

If a distance D2 between the anode 306 and the electron-emitting film 305 is reduced in view of these problems, the beam diameter of emitted electrons is decreased to some extent and the anode voltage required for electron emission is lowered. In this case, however, the energy of emitted electrons is also lowered and therefore it becomes difficult to have the phosphor emit light having sufficient brightness.

An example of the foregoing edge emitter type electron-emitting devices is shown in Fig. 17.

The electron-emitting device in this example has a

construction where a cathode 312 is sandwiched between two gate electrodes 314, with insulating layers 313 being inserted between the cathode 312 and the gate electrodes 314. With this construction, the two gate
5 electrodes 314 apply positive voltages ($0 < |V_{g1}| \leq |V_{g2}|$) to the cathode 312, thereby increasing the amount of electrons emitted from the cathode 312. In this case, however, the beam diameter of emitted electrons tends to be increased.

10 The present invention has been made in the light of the above-mentioned problems of the conventional techniques, and an object of the present invention is to provide an electron-emitting device, an electron source, and an image-forming apparatus, which are
15 driven at low voltage, have uniform electron-emitting characteristics, produce electron beams having small diameters, have simple constructions, and are easy to be manufactured.

20 The present invention which has been attained to solve the above-mentioned problems is given below:

25 That is, an electron-emitting apparatus of the present invention is characterized in that: the apparatus comprises: an electron-emitting device including a first electrode, a second electrode that is provided so as to be insulated from the first electrode, and an electron-emitting film connected to the second electrode; and

an anode provided at a predetermined distance from the electron-emitting film; and that

the first electrode, the second electrode, and the electron-emitting film oppose the anode; a distance
5 between the anode and the electron-emitting film is longer than a distance between the anode and the second electrode; and a distance between the anode and the first electrode is longer than the distance between the anode and the electron-emitting film.

10 Further, the electron-emitting device of the present invention is characterized in that: the device comprises: a first electrode arranged on a surface of a substrate, an insulating layer arranged on the first electrode, a second electrode arranged on the
15 insulating layer, and an electron-emitting film arranged on the second electrode, and that the second electrode has two side surfaces that oppose each other in a direction parallel to the surface of the substrate; and the electron-emitting film is arranged
20 so as to be shifted toward one of the two side surfaces.

An electron source is formed by arranging a plurality of the above electron-emitting devices, and is characterized in that the electron source emits
25 electrons using at least one of the plurality of electron-emitting devices according to an input signal.

An image-forming apparatus is characterized by

comprising the above electron source, and an image forming member on which an image is formed by irradiation with electrons emitted from the electron source.

5 With employment of the electron-emitting device according to the present invention, an electron beam, which is driven at a low voltage; is easy to produce; and has a small beam diameter, can be obtained, and in addition an electron source and an image-forming
10 apparatus, which have uniform electron-emitting characteristics with high definition, and are stable for a long time period, can be realized.

BRIEF DESCRIPTION OF THE DRAWINGS

15 Fig. 1 is a schematic cross-sectional view showing the construction of an electron-emitting device to which the present invention is applied;

 Fig. 2 is a schematic plain view showing the construction of the electron-emitting device to which
20 the present invention is applied;

 Fig. 3 is a schematic cross-sectional view showing a state where electrons are emitted from the electron-emitting device to which the present invention is applied;

25 Fig. 4 is a schematic cross-sectional view showing a state where the emission of electrons from the electron-emitting device, to which the present

invention is applied, is prohibited;

Figs. 5A, 5B, 5C, 5D, 5E, 5F and 5G show an example method of manufacturing the electron-emitting device to which the present invention is applied;

5 Fig. 6 is a schematic view showing the construction of an electron source having passive matrix configuration according to an embodiment of the present invention;

10 Fig. 7 is a schematic view showing the construction of an image-forming apparatus that uses the electron source having the passive matrix configuration according to the embodiment of the present invention;

15 Figs. 8A and 8B each show a fluorescent film in the image-forming apparatus according to the embodiment of the present invention;

 Fig. 9 is a schematic cross-sectional view of an electron-emitting device according to a fourth embodiment;

20 Figs. 10A, 10B, 10C, 10D, 10E and 10F show an example method of manufacturing the electron-emitting device according to the fourth embodiment;

25 Fig. 11 is a schematic cross-sectional view of an electron-emitting device according to a fifth embodiment;

 Fig. 12 is a schematic cross-sectional view of an electron-emitting device according to a sixth

embodiment;

Figs. 13A, 13B, 13C, 13D, 13E, 13F, 13G and 13H show an example method of manufacturing the electron-emitting device according to the sixth embodiment;

5 Fig. 14 is a schematic cross-sectional view of an electron-emitting device according to the seventh embodiment;

Fig. 15 is a schematic plain view of the electron-emitting device according to the seventh embodiment;

10 Fig. 16 is a schematic cross-sectional view of a diode type electron-emitting device among FE type electron-emitting devices;

Fig. 17 is a schematic cross-sectional view of an edge emitter type electron-emitting device among the FE type electron-emitting devices;

15 Figs. 18A and 18B are schematic cross-sectional views used to explain the construction of the electron-emitting device of the present invention;

Fig. 19 is a schematic diagram illustrating a construction of a fiber whose main ingredient is carbon; and

20 Fig. 20 is a schematic diagram illustrating another construction of the fiber whose main ingredient is carbon.

25

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The preferred embodiment of the present invention

will be exemplarily described in detail below with reference to the drawings. Note that the sizes, materials, shapes, relative positions, and other aspects of components described below should be

5 appropriately changed according to the construction and various conditions of an apparatus to which the present invention is applied. Therefore, there is no intention to limit the scope of the present invention to the following description.

10 An electron-emitting device to which the present invention is applied has a characteristic that a first electrode, an electron-emitting film, and a second electrode oppose an anode, a step is formed between a surface of the first electrode opposing the anode and a
15 surface of the electron-emitting film opposing the anode, another step is formed between the surface of the electron-emitting film opposing the anode and a surface of the second electrode opposing the anode, a distance from the surface of the first electrode
20 opposing the anode to the anode is longer than that from the surface of the electron-emitting film opposing the anode to the anode, and a distance from the surface of the electron-emitting film opposing the anode to the anode is longer than that from the surface of the
25 second electrode opposing the anode to the anode. That is, the electron-emitting device is characterized in that it has a step-like construction.

As is apparent from this, the electron-emitting device to which the present invention is applied can be constructed merely by laminating the components. This means that the electron-emitting device is easy to be
5 manufactured and the construction thereof is easy to be controlled. As a result, the uniformity of the electron-emitting characteristic of the electron-emitting device is increased.

Also, the electron-emitting device to which the
10 present invention is applied is characterized in that it is a triode device where the emission of electrons from the electron-emitting film is caused by the anode to which a given voltage is applied and the emitted electrons are controlled by the first electrode
15 functioning as a modulation electrode.

In the electron-emitting device to which the present invention is applied, the first electrode on the substrate functions as a modulation electrode. This makes it possible to apply a high voltage to the
20 anode, so that emitted electrons strike a phosphor with energy that is enough to have the phosphor emit light. As a result, light having sufficient brightness is emitted from the phosphor.

Also, by applying a voltage, which is lower than
25 that applied to the electron-emitting film, to the electrode used as a modulation electrode, the strength of an electric field applied to an electron-emitting

region of the electron-emitting film can be decreased without difficulty. This makes it possible to drive the electron-emitting device, to which the present invention is applied, at low voltage.

5 Fig. 2 is a schematic plain view showing the construction of the electron-emitting device according to an embodiment of the present invention, while Fig. 1 is a schematic diagram of an electron-emitting apparatus in which an anode is disposed so as to oppose
10 the electron-emitting device. Here, Fig. 1 is a schematic cross-sectional view taken along the line 1-1 in Fig. 2. Also, Fig. 3 is a schematic cross-sectional view showing a state where electrons are emitted from the electron-emitting film in the electron-emitting
15 apparatus. Further, Fig. 4 is a schematic cross-sectional view showing a state where the emission of electrons from the electron-emitting film is prohibited in the electron-emitting apparatus.

 In Figs. 1 and 2, reference numeral 11 represents
20 a substrate; numeral 12, a first electrode; numeral 13, an insulating layer; numeral 14, a second electrode; numeral 15, an electron-emitting film that is a conductive film; numeral 16, an anode; symbol W1, the width of the step of the second electrode; and symbol
25 L1, an electrode length.

 The width W1 of the step of the second electrode is appropriately set according to the materials and

resistance of the components, the work function and driving voltage of the material of the second electrode 14, and the required shape of the electron beam to be emitted. The width W_1 is usually set in a range of
5 several nm to several hundred μm , and preferably in a range of several ten nm to several μm . Also, the electrode length L_1 is appropriately set according to the materials and resistance value of the components and the position of the electron-emitting device. The
10 electrode length L_1 is usually set in a range of several hundred nm to several μm , and preferably in a range from several nm to several hundred μm .

Symbol V_a denotes a voltage applied to the anode 16, which is a positive electrode, by a first voltage
15 applying means. The potential applied to the anode 16 is higher than those applied to the first electrode 12 and the second electrode 14. Symbol V_b represents a voltage applied between the first electrode 12 and the second electrode 14 by a second voltage applying means.
20 In more detail, $V_b[V] = \text{potential}[V]$ of the first electrode 12 - $\text{potential}[V]$ of the second electrode 14. The electric field applied to the electron-emitting film 15 is formed by the voltages V_a and V_b .

Fig. 3 is a schematic cross-sectional view showing
25 an example driving method where electrons are emitted from the electron-emitting device according to this embodiment. In this drawing, reference numeral 17a

represents an equipotential surface formed in the vicinity of the electron-emitting film 15 during the electron emission. This drawing relates to a case where the voltage V_b is set at 0V during the electron emission. The shape of the equipotential surface 17a is determined by the magnitude of the voltage V_a and the thickness and width of each component of the electron-emitting device. However, the electric field applied to the end portion of the electron-emitting film 15 is greater than those applied to other portions thereof, so that electrons are emitted only from the end portion. As a result, the beam diameter of the emitted electrons becomes small. In particular, the electric field applied to a portion of the electron-emitting film 15 in the vicinity of the step portion of the second electrode is extremely small. Also, the thickness and width of each component of the electron-emitting devices may be freely set at values suitable for the application purpose.

Also, if the voltage V_b is set at 0V, there may be cases where no electrons are emitted, depending on respective parameters such as the material of the electron-emitting film 15, the shape of the second electrode 14, the distance between the anode 16 and the electron-emitting film 15, and the potential applied to the anode 16. Therefore, with the construction of the electron-emitting device according to this embodiment,

the strength of the electric field applied to the end portion of the electron-emitting film 15 is increased not by setting the voltage V_b at 0V but by setting the potential of the first electrode 12 at a value higher
5 than that of the potential of the second electrode 14. This relaxes the requirements that need to be satisfied by the foregoing parameters.

As a result, with the construction of the electron-emitting device of the present invention, the
10 voltage V_b is not limited to 0V. That is, when the electron-emitting device of the present invention is driven, it is preferable that the potential of the first electrode 12 is set at a value higher than that of the potential of the second electrode 14. As a
15 result, during the driving of the electron-emitting device of the present invention, the voltage (V_b) applied between the first and second electrodes satisfies a condition " $V_b \geq 0[V]$ ", or preferably a condition " $V_b > 0[V]$ ".

20 Also, Fig. 4 is a schematic cross-sectional view showing an example driving method where the electron emission from the electron-emitting device of the present invention is prohibited. In this drawing, reference numeral 17b represents an equipotential
25 surface formed in the vicinity of the electron-emitting film 15. In this example, the potential applied to the second electrode 14 is higher than that applied to the

first electrode 12 ($V_b < 0V$). The shape of the equipotential surface 17b is determined by the magnitudes of the voltages V_a and V_b , a distance D_1 , and the thickness and width of each component. Because
5 the voltage applied to the second electrode 14 is higher than that applied to the first electrode 12 in this example, the equipotential surface in the vicinity of the end portion of the electron-emitting film 15 is lifted toward the anode 16 and the electric field
10 applied to the end portion of the electron-emitting film 15 is weakened. As a result, no electrons are emitted from the electron-emitting film 15.

Also, a potential difference V_b required to prevent the electron emission from the electron-emitting film 15 is determined by the magnitude of the
15 voltage V_a , the distance D_1 , and the thickness of each component arranged between the substrate and the electron-emitting film 15. The potential difference can be reduced by freely selecting values that are
20 suitable for an application purpose.

Also, in the foregoing electron-emitting device of the present invention, as described by referring to Fig. 3, a surface part (convex portion) of the second electrode 14, whose distance to the anode electrode 16
25 is shorter than the distance between the electron-emitting film 15 and the anode electrode 16, increases the strength of the electric field applied to the end

portion of the electron-emitting film 15. Thus, the strength of the electric field applied thereto becomes greater than those of the electric fields applied to other portions of the electron-emitting film 15.

5 Therefore, it is most preferable that the distance between the anode 16 and part of the surface of the second electrode 14 is shorter than the distance between the anode 16 and the surface of the end portion of the electron-emitting film 15.

10 The electron-emitting device of the present invention, however, may have a construction where the distance between the second electrode 14 and the substrate 11 is shorter than that between the electron-emitting film 15 and the substrate 11 (the distance
15 between the electron-emitting film 15 and the anode electrode 16 is shorter than that between the second electrode 14 and the anode electrode 16). That is, as shown in Fig. 18A, the electron-emitting device may have a construction where the first electrode 12 is
20 arranged on the surface of the substrate 11, the insulating layer 13 is arranged on the first electrode 12, the second electrode 14 is arranged on the insulating film 13, and the electron-emitting film 15 is arranged on the second electrode 14. Note that
25 symbol 17c in Fig. 18A denotes an equipotential surface formed in the vicinity of an electron-emitting portion. Similarly to the case of the electron-emitting device

shown in Fig. 3, the driving voltage (voltage applied between the first electrode and the second electrode) V_b in Fig. 18A satisfies the condition " $V_b \geq 0[V]$ ", or preferably the condition " $V_b > 0[V]$ ".

5 It should be noted here that in the case of the construction shown in Fig. 18A, like the construction shown in Fig. 2 and 3, the electron-emitting film 15 is (eccentrically) arranged adjacent to one end portion of the second electrode 14. In other words, the electron-emitting film 15 is arranged so as to be shifted toward
10 one of two side surfaces (edges) of the second electrode 14 that are opposite to each other in a direction substantially parallel to the surface of the substrate. Also, in other words, the electron-emitting
15 film 15 is arranged so as to be shifted toward one of two end portions of the second electrode 14 that are opposite to each other in a direction substantially parallel to the surface of the substrate.

 If the electron-emitting film 15 is arranged to
20 entirely cover a surface of the second electrode 14 as shown in Fig. 18B, electrons are emitted from both ends of the electron-emitting film 15 and therefore the diameter of an electron beam is increased. Note that symbol 17d in Fig. 18B denotes an equipotential surface
25 formed in the vicinity of an electron-emitting region.

 An example method of manufacturing the foregoing electron-emitting device of the present invention is

described below with reference to Figs. 1 and 5A to 5G.

First, a lamination member is produced by sufficiently cleaning the surfaces of quartz glass, glass in which the amount of impurities, such as Na, is reduced, a soda lime glass, a silicon substrate, or the like, and then laminating SiO_2 film thereon with a sputtering method or the like. Alternatively, an insulating substrate is produced using ceramics such as alumina. The lamination member or the insulating substrate is used as the substrate 11. Then, the first electrode 12 is laminated on the substrate 11.

In general, the first electrode 12 has conductivity and is formed with a general vacuum layer formation technique, such as a vapor deposition method or a sputtering method, or a photolithography method. The material of the first electrode 12 is, for instance, appropriately selected from a group of carbon and a carbon compound consisting of metals (such as Be, Mg, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Al, Cu, Ni, Cr, Au, Pt, and Pd), their alloys, a carbide (such as TiC , ZrC , HfC , TaC , SiC , and WC), a boride (such as HfB_2 , ZrB_2 , LaB_6 , CeB_6 , YB_6 , and GdB_6), a nitride (such as TiN , ZrN , and HfN), a semiconductor (such as Si and Ge), an organic highpolymer material, an amorphous carbon, graphite, diamond like carbon, carbon in which diamond is dispersed, and a carbon compound. The thickness of the first electrode 12 is set in a range of several ten

nm to several μm , and preferably in a range of several hundred nm to several μm .

Next, the insulating layer 13 is stacked on the first electrode 12. The insulating layer 13 is formed with a general vacuum layer formation technique, such as a sputtering method, a CVD method, or a vacuum evaporation method. The thickness of the insulating layer 13 is set in a range of several nm to several μm , and preferably in a range of several ten nm to several hundred nm. It is preferable that the insulating layer 13 is made of a material, such as SiO_2 , SiN , Al_2O_3 , CaF_2 , and undoped diamond, that has a high withstand voltage and is resistant to a high electric field.

Further, as shown in Fig. 5A, the second electrode 14 is stacked on the insulating layer 13. Like the first electrode 12, the second electrode 14 has conductivity and is formed with a general vacuum layer formation technique, such as a vapor deposition method or a sputtering method, or a photolithography method. The material of the second electrode 14 is, for instance, appropriately selected from a group consisting of metals (such as Be, Mg, Ti, Zr, Hf, V, Nb, Ta, Mo, W, Al, Cu, Ni, Cr, Au, Pt, and Pd), their alloys, a carbide (such as TiC , ZrC , HfC , TaC , SiC , and WC), a boride (such as HfB_2 , ZrB_2 , LaB_6 , CeB_6 , YB_4 , and Gd_2B_4), a nitride (such as TiN , ZrN , and HfN), a semiconductor (such as Si and Ge), and an organic

highpolymer material. The thickness of the second electrode 14 is set in a range of several nm to several ten μm , and preferably in a range of several ten nm to several μm .

5 It should be noted here that it does not matter whether the first and second electrodes 12 and 14 are made of the same material or different materials. Also, it does not matter whether these electrodes 12 and 14 are formed with the same method or different
10 methods.

Next, as shown in Fig. 5B, a mask pattern 18 is formed using a photolithography technique.

Following this, the lamination structure shown in Fig. 5C is obtained by partially removing the
15 insulating layer 13 and the second electrode 14 from the lamination device including the first electrode 12. Note that it does not matter whether the etching operation is terminated before the first electrode 12 is etched or is continued until the first electrode 12
20 is partially etched. The etching method used in this etching step is appropriately selected according to the materials of the insulating layer 13 and the second electrode 14.

Next, the mask pattern 18 is peeled off and then
25 another mask pattern 19 is formed using a photolithography technique as shown in Fig. 5D.

Then, as shown in Fig. 5E, a part of the second

electrode 14 is removed to obtain a step-like shape of the second electrode 14. This etching step needs to be terminated before the second electrode 14 is completely etched from the top surface to the bottom surface.

5 Following this, as shown in Fig. 5F, the electron-emitting film 15 is disposed using a general vacuum layer formation technique, such as a vapor deposition method or a sputtering method, or a photolithography method. The material of the electron-emitting film 15
10 is, for instance, appropriately selected from a group consisting of graphite, fullerene, carbon nanotubes, graphite nanofibers, diamond like carbon, carbon in which diamond is dispersed. It is preferable that the electron-emitting film 15 is made of a thin diamond
15 film or diamond like carbon having a low work function. It is particularly preferable that the electron-emitting film 15 is made of fiber comprises carbon as a main ingredient (referred to as "fibrous carbon") that easily emit electrons in a low electric field, such as
20 graphitic nanofibers or carbon nanotubes. The thickness of the electron-emitting film 15 is set in a range of several nm to several μm , and preferably in a range of several nm to several hundred nm.

 If the fibers whose main ingredients are carbon
25 are used as the material of the electron-emitting film 15, the electron-emitting film 15 becomes an aggregate of a plurality of fibers whose main ingredients are

carbon.

The fibers whose main ingredients are carbon has a threshold electric field of several V/ μ m. Examples of the aggregate of fibers whose main ingredients are carbon are shown in Figs. 19 and 20. In each drawing, the carbon configuration captured at an optical microscope level ($\sim 1000\times$ magnification) is schematically shown in the left area, the carbon configuration captured at a scanning electron microscope (SEM) level ($\sim 30000\times$ magnification) is schematically shown in the center area, and the carbon configuration captured at a transmission electron microscope (TEM) level ($\sim 1000000\times$ magnification) is schematically shown in the right area.

A graphene that has a cylindrical shape as shown in Fig. 19 is called a carbon nanotube (a cylindrical graphene having a multi-layered structure is called a multi-wall nanotube). In particular, in the case of a shape where the tip of the tube is expanded, the threshold value is reduced to a minimal level.

Fig. 20 shows a fiber that may be produced at a relatively low temperature to include carbon as its main ingredient. The fiber shown in Fig. 20 is a graphene layered product. Therefore, this fiber is called a "graphite nanofiber" in some cases, although the ratio of an amorphous structure increases depending on the temperature. In more detail, the graphite

nanofiber is a fibrous substance in which graphens are layered (laminated) in the longitudinal direction thereof (in the axial direction of the fiber). In other words, as shown in Fig. 20, the graphite
5 nanofiber is a fibrous substance in which plurality of graphenes are layered (laminated) so as not to be parallel to the fiber axis.

On the other hand, the carbon nanotube is a fibrous substance in which graphens are arranged (in
10 cylindrical shape) around the longitudinal direction of the fiber (the axial direction of the fiber). In other words, the carbon nanotube is a fibrous substance in which graphenes are arranged substantially parallel to the fiber axis.

15 It should be noted here that a single plane of graphite is referred to as a "graphene" or a "graphene sheet". In more detail, the graphite has a construction where regular hexagons formed by carbon atoms having covalent bonds attributed to sp^2 hybrid
20 orbital are arranged to form a carbon plane and a plurality of carbon planes having such a construction are laminated with a distance of 3.354\AA therebetween. Each of these carbon planes is referred to as a "graphene" or a "graphene sheet".

25 In either case of these fibers whose main ingredients are carbon, the threshold value concerning electron emission is around $1\text{V}-10\text{V}/\mu\text{m}$. Therefore,

these fibers are both suitable as the material of the electron-emitting film 15 of the present invention.

In particular, an electron-emitting device using an aggregate of graphite nanofibers causes electron
5 emission in a low electric field, achieves large emission current, is easy to be manufactured, and has a stable electron-emitting characteristic. Also, in an electron-emitting apparatus, light-emitting apparatus, and image display apparatus using the graphite
10 nanofibers, stable electron emission is performed without maintaining the inside of these apparatuses in a ultra-high vacuum state, unlike conventional electron-emitting devices. Also, electrons are emitted in a low electric field, so that an apparatus with a
15 high degree of reliability is manufactured without difficulty.

The stated fibers whose main ingredients are carbon can be produced by dissolving a hydrocarbon gas using a catalyst (a material promoting the deposition
20 of carbon). The carbon nanotube differs from the graphite nanofiber in the type of a catalyst and the dissolving temperature.

As to the material of the catalyst, a material such as Fe, Co, Pd, or Ni, or an alloy of materials
25 selected therefrom may be used as a nucleus for forming a fiber whose main ingredient is carbon.

In particular, in the case of Pd or Ni, it is

possible to produce a graphite nanofiber at a low temperature (400°C or higher). If a carbon nanotube is produced using Fe or Co, however, the temperature needs to be increased to 800°C or higher. Because the
5 production of a graphite nanofiber using Pd or Ni is possible at a low temperature, these materials are preferable in terms of the effects on other components and the manufacturing cost.

Further, by utilizing a characteristic that oxides
10 are reduced by hydrogen at a low temperature (room temperature) in the case of Pd, the nucleus may be formed using palladium oxide.

If the palladium oxide is subjected to a hydrogen reduction process, it becomes possible to form an
15 initial aggregation nucleus at a relatively low temperature (200°C or lower) without using a conventional nucleus formation technique, such as the heat aggregation of a thin metal film or the generation and vapor deposition of ultra-fine particles.

20 As the hydrocarbon gas described above, there may be used a hydrocarbon gas (such as ethylene, methane, propane, or propylene), CO gas, CO₂ gas, or a steam of an organic solvent (such as ethanol or acetone), for instance.

25 Finally, the mask pattern 19 is peeled off as shown in Fig. 5G. In this manner, the electron-emitting device of the present invention is

manufactured.

The electron-emitting device shown in Fig. 1 that has been described above as an example of the present invention has a construction where the first electrode
5 12 is disposed on the substrate 11 and a convex portion composed of the insulating layer 13, the second electrode 14, and the electron-emitting film 15 is formed on a part of the surface of the first electrode 12. Also, a part of the second electrode 14 has a
10 step-like shape and the electron-emitting film 15 is disposed on the lower surface of the second electrode 14. However, the electron-emitting device of the present invention is not limited to this construction and the second electrode 14 may be composed of a
15 plurality of layers. Also, so long as the layers are electrically connected and have the same potential, it is not required that these layers are successively laminated on each other. That is, at least one different component, such as the electron-emitting film
20 15 or the insulating layer 13, may be inserted between the second electrode layers. Further, the first electrode 12 may be disposed only in an area of the substrate 11 in which the convex portion is not formed. Also, the surface of the electron-emitting film 15 may
25 have any one of a polygon shape, a slit shape, at least one part of a circle shape, and at least one part of an ellipse shape.

Example applications of the electron-emitting device of the present invention are described below.

For instance, an electron source or an image-forming apparatus may be constructed by arranging a plurality of the electron-emitting devices of the present invention on a substrate.

An electron source produced by arranging a plurality of the electron-emitting devices of the present invention is described below with reference to Fig. 6. In this drawing, symbol 121 denotes an electron source substrate, numeral 122 X-directional wiring, numeral 123 Y-directional wiring, numeral 124 the electron-emitting devices according to the present invention, and numeral 125 connection wiring.

There are m X-directional wiring 122 ($Dx1$, $Dx2$, ..., Dxm) that are made of a conductive metal or the like using a vacuum evaporation method, a printing method, a sputtering method, or the like. The material, thickness, and width of each wire is determined as appropriate. There are n Y-directional wiring 123 ($Dy1$, $Dy2$, ..., Dyn) that are produced in the same manner as the X-directional wiring 122. An interlayer insulating layer (not shown) is provided between the m X-directional wiring 122 and the n Y-directional wiring 123 so as to electrically insulate these wiring. Here, m and n are each a positive integer.

The interlayer insulating layer (not shown) is made of SiO_2 or the like using a vacuum evaporation method, a printing method, a sputtering method, or the like. For instance, the interlayer insulating layer having a desired shape is produced to cover the entire or a part of the surface of the electron source substrate 121 on which the X-directional wiring 122 have been formed. In particular, the thickness, material, and production method of the interlayer insulating layer are determined as appropriate so that the interlayer insulating layer is resistant to potential differences at the intersections of the X-directional wiring 122 and the Y-directional wiring 123. The X-directional wiring 122 and the Y-directional wiring 123 are extended to the outside as external terminals.

A pair of electrode layers (not shown) constituting the electron-emitting device 124 are electrically connected to the m X-directional wiring 122 and the n Y-directional wiring 123 by the connection wiring 125 made of a conductive metal or the like.

The X-directional wiring 122, the Y-directional wiring 123, the connection wiring 125, and the pair of device electrodes may be made of partially or completely the same component devices or made of different devices. The foregoing wiring are made of

materials appropriately selected from the foregoing materials of the first electrode 12 and the second electrode 14 that are the device electrodes. If the same material is used to produce the device electrodes and the wiring, the wiring connected to the device electrodes may also be called device electrodes. Also, the device electrodes may be used as wiring electrodes.

To select the rows of the electron-emitting device 124 arranged in the X-direction, a scanning signal applying means (not shown) for applying a scanning signal is connected to the X-directional wiring 122. On the other hand, to modulate each column of the electron-emitting device 124 arranged in the Y-direction according to an input signal, a modulation signal generating means (not shown) is connected to the Y-directional wiring 123. The driving voltage applied to each electron-emitting device is supplied as the difference voltage between the scanning signal and the modulation signal applied to the electron-emitting device.

The above-mentioned construction makes it possible to select respective electron-emitting devices and independently drive the selected electron-emitting devices using a passive matrix wiring. An image-forming apparatus formed using an electron source having the foregoing passive matrix configuration is described below with reference to Fig. 7. This drawing

is a schematic diagram showing an example of a display panel of the image-forming apparatus.

Referring to Fig. 7, reference numeral 121 represents a substrate of the electron source on which
5 a plurality of the electron-emitting devices 124 of the present invention are arranged in the manner described above, numeral 131 a rear plate to which the electron source substrate 121 is secured, numeral 136 a face
10 plate having a construction where a fluorescent film 134 (a phosphor), a metal back 135, and the like serving as image forming members are formed on the internal surface of a glass substrate 133, and numeral 132 a support frame. An envelope 137 is formed using the rear plate 131, the support frame 132, and the face
15 plate 136 by applying frit glass or the like to their connection portions and then baking, in the air or a nitrogen atmosphere, the foregoing components at 400°C to 500°C for 10 minutes or longer to seal the components.

20 The envelope 137 is, as described above, formed by the face plate 136, the support frame 132, and the rear plate 131. Because the rear plate 131 is provided to mainly reinforce the strength of the electron source substrate 121, the rear plate 131 is not required if
25 the electron source substrate 121 itself has sufficient strength. In this case, the support frame 132 may be directly sealed to the electron source substrate 121 to

form the envelope 137 using the face plate 136, the support frame 132, and the electron source substrate 121. Also, by inserting a support member called a spacer (not shown) between the face plate 136 and the rear plate 131, the envelope 137 may be made to be sufficiently strong against the atmospheric pressure.

It should be noted here that in the image-forming apparatus using the electron-emitting devices according to the present invention, a phosphor(the fluorescent film 134) is arranged in alignment over the electron-emitting devices 124 in consideration of the trajectory of emitted electrons. Figs. 8A and 8B are each a schematic diagram of the fluorescent film 134 used in the panel. In the case where the fluorescent film 134 is a color fluorescent film, the fluorescent film 134 is composed of phosphors 142 and black conductive members 141 that are called a black stripe (see Fig. 8A) or a black matrix (see Fig. 8B) depending on the arrangement style of the phosphors.

The image-forming apparatus according to the present invention may be used as a display apparatus for television broadcasting, a display apparatus for a video conference system, a computer or the like. Furthermore, the image-forming apparatus according to the present invention may be used as an image-forming apparatus for a laser printer comprising a photosensitive drum or the like.

<Embodiments>

Embodiments of the present invention are described in detail below.

<First Embodiment>

5 Fig. 2 is a plan view of the electron-emitting apparatus of the first embodiment, Fig. 1 is a cross sectional view of the electron-emitting apparatus, and Figs. 5A to 5G show a method of manufacturing the electron-emitting apparatus. The method of
10 manufacturing the electron-emitting apparatus of this embodiment is described in detail below.

(Step 1)

 First, as shown in Fig. 5A, with a sputtering method, the first electrode 12 that is an Al film
15 having a thickness of 300 nm, the insulating layer 13 that is an SiO₂ film having a thickness of 100 nm, and the second electrode 14 that is a Ta film having a thickness of 400 nm are stacked in this order on the substrate 11 that is a sufficiently cleaned quartz
20 glass.

(Step 2)

 Next, as shown in Fig. 5B, a photomask pattern of a positive photoresist (AZ1500 manufactured by Clariant) is formed by spin coating, and is exposed to
25 light and developed with a photolithography method to obtain a mask pattern 18. Then, as shown in Fig. 5C, dry etching is performed using CF₄ gas from above of the

mask pattern 18 functioning as a mask, so that the insulating layer 13 and the second electrode 14 are etched. This etching operation is terminated before the first electrode 12 is also processed.

5 (Step 3)

Following this, the mask pattern 18 is peeled off. Then, as shown in Fig. 5D, a photomask pattern of a positive photoresist (AZ1500 manufactured by Clariant) is formed by spin coating, and is exposed to light and developed with a photolithography method to obtain a mask pattern 19. Then, dry etching is performed using CF_4 gas from above of the mask pattern 19 functioning as a mask to obtain the step-like shape of the second electrode 14 shown in Fig. 5E. The difference in height between the upper surface and lower surface of the second electrode 14 is set at 300 nm, the electrode length L_1 is set at 100 μm , and the width of the lower surface is set at 0.5 μm .

(Step 4)

20 Next, as shown in Fig. 5F, a diamond like carbon film having a thickness of 100 nm is formed as the electron-emitting film 15 using a CVD (chemical vapor deposition) method.

Finally, the mask pattern 19 used as a mask is completely removed to obtain the electron-emitting device of this embodiment shown in Fig. 5G.

Electron emission is performed by arranging the

thus-manufactured electron-emitting device in the manner shown in Fig. 3. The applied voltage V_a is set at 10kV and the distance D_1 between the electron-emitting film 15 and the anode 16 is set at 2 mm.

5 Here, an electrode formed by applying a phosphor is used as the anode 16. Under these condition, electron emission is performed and the electron beam diameter is observed. The term "electron beam diameter" refers to a size of a beam area in which is observed at least 10%
10 of the peak brightness of the light emitted from the phosphor. The electron beam diameter becomes 80 μm /200 μm (x/y) in this embodiment.

Also, when voltages are applied so that the potential of the second electrode 14 becomes higher
15 than that of the first electrode 12 and the difference between these voltages becomes 4V (which is to say $V_b=4V$), the electron-emitting device of this embodiment does not emit any electrons, as shown in Fig. 4. As is
apparent from this, it is possible to drive the
20 electron-emitting device of this embodiment at a very low voltage.

<Second Embodiment>

A schematic cross-sectional view of the electron-emitting device manufactured in the second embodiment
25 is shown in Fig. 1. In this embodiment, the second electrode layer 14 of the first embodiment is produced by laminating a Ta film and an Al film to prevent the

unevenness of the lower surface of the second electrode layer 14 having a step-like shape due to the device.

The following description centers on the characteristic points of this embodiment and therefore the same points
5 as in the first embodiment are omitted.

Similarly to the first embodiment, after the first electrode 12 and the insulating layer 13 are laminated on the substrate 11, an Al film having a thickness of 100 nm and a Ta film having a thickness of 300 nm are
10 stacked in this order as the second electrode 14.

Following this, like in the first embodiment, a mask pattern 18 is formed, the Ta film of the second electrode 14 and the insulating layer 13 are dry etched using CF_4 gas, and the Al film of the second electrode
15 14 is dry etched using Cl_2 gas. This etching operation is terminated before the first electrode 12 is also processed.

Then, like in the first embodiment, the mask pattern 18 is peeled off, another mask pattern 19 is
20 formed, and the second electrode 14 is processed using CF_4 gas to obtain the step-like shape of the second electrode 14. It is impossible to remove the Al film using CF_4 gas, so that the thickness of each film of the second electrode 14 becomes even and the unevenness of
25 the lower surface of the second electrode 14 is prevented.

Other aspects of this embodiment are the same as

those of the first embodiment and so are omitted.

<Third Embodiment>

A schematic cross-sectional view of the electron-emitting device manufactured in the third embodiment is shown in Fig. 1. In this embodiment, the applied voltage V_a is increased so as to improve the current amounts of emitted electrons. The following description centers on the characteristic points of this embodiment and therefore the same points as in the aforementioned embodiments are omitted.

In this embodiment, the voltage V_a applied to drive the electron-emitting device of the first embodiment is set at 15kV and the distance D_1 between the electron-emitting film 15 and the anode 16 is set at 2 mm.

The electron-emitting device performs electron emission by means of the electric field formed by the anode voltage, so that the increased anode voltage improves the current amounts of the emitted electrons in this embodiment. At the same time, however, the area from which electrons are emitted is also extended and therefore the beam diameter of the emitted electrons is increased.

<Fourth Embodiment>

Fig. 9 is a schematic cross-sectional view of the electron-emitting device manufactured in this embodiment, and Figs. 10A to 10F show a method of

manufacturing the same. In this embodiment, the electron-emitting film 15 is sandwiched between layers of the second electrode 14. The electron-emitting device having this construction can be manufactured more easily. The method of manufacturing the electron-emitting device of this embodiment is described in detail below.

(Step 1)

First, as shown in Fig. 10A, the substrate 11 is prepared by sufficiently cleaning a quartz glass. Following this, with a sputtering method, the first electrode 12 that is an Al film having a thickness of 300 nm, the insulating layer 13 that is an SiO₂ film having a thickness of 100 nm, a second electrode layer 14a that is a Ta film having a thickness of 100 nm, the electron-emitting film 15 that is a diamond like carbon film having a thickness of 100 nm, and a second electrode layer 14b that is a Ta film having a thickness of 200 nm are stacked onto the substrate 11 in this order.

(Step 2)

Next, as shown in Fig. 10B, a photomask pattern of a positive photoresist (AZ1500 manufactured by Clariant) is formed by spin coating, and is exposed to light and developed with a photolithography method to obtain a mask pattern 18. Then, as shown in Fig. 10C, dry etching is performed using CF₄ gas from above of the

mask pattern 18 functioning as a mask, so that the insulating layer 13, the second electrode layer 14a, the electron-emitting film 15, and the second electrode layer 14b are etched. This etching operation is
5 terminated before the first electrode 12 is also processed.

(Step 3)

Following this, the mask pattern 18 is peeled off. Then, as shown in Fig. 10D, a photomask pattern of a
10 positive photoresist (AZ1500 manufactured by Clariant) is formed by spin coating, and is exposed to light and developed with a photolithography method to obtain a mask pattern 19. Then, dry etching is performed using CF_4 gas from above of the mask pattern 19 functioning as
15 a mask, so that the second electrode layer 14b is etched and the electron-emitting film 15 obtains an exposed portion as shown in Fig. 10E.

(Step 4)

Finally, the mask pattern 19 used as a mask is
20 completely removed to obtain the electron-emitting device of this embodiment shown in Fig. 10F. Similarly to the case of the electron-emitting device of the first embodiment, the electrode length L1 of this electron-emitting device is set to 100 μm .

25 The thus-manufactured electron-emitting device is driven under a condition where $V_a=10kV$, $V_b=0V$, and $D1=2 mm$. The electron emission performed in this case

achieves an electron-emitting characteristic that is almost the same as in the case of the electron-emitting device of the first embodiment.

<Fifth Embodiment>

5 Fig. 11 is a schematic cross-sectional view of the electron-emitting device manufactured in this embodiment. This embodiment relates to a construction where an insulating layer 13b is inserted between the electron-emitting film 15 and the second electrode
10 layer 14b of the electron-emitting device of the fourth embodiment. It will become apparent from this embodiment that there occurs no change in the characteristics of the electron-emitting device even with the construction where the insulating layer 13b is
15 sandwiched between the components. The following description centers on the characteristic points of this embodiment and therefore the same points as in the above-mentioned embodiments are omitted.

 Similarly to the fourth embodiment, the first
20 electrode 12, the insulating layer 13a, the second electrode layer 14a, and the electron-emitting film 15 are laminated on the substrate 11. Then, the insulating layer 13b that is an SiO₂ film having a
 thickness of 100 nm and the second electrode layer 14b
25 that is a Ta film having a thickness of 100 nm are stacked in this order onto the electron-emitting film 15.

Following this, like in the fourth embodiment, the mask pattern 18 is formed and dry etching is performed for the insulating layer 13a, the second electrode layer 14a, the electron-emitting film 15, the
5 insulating layer 13b, and the second electrode layer 14b. This etching operation is terminated before the first electrode layer 12 is also processed.

Then, like in the fourth embodiment, the mask pattern 18 is peeled off, another mask pattern 19 is
10 formed, and the second electrode layer 14b and the insulating layer 13b are subjected to dry etching to obtain an exposed portion of the electron-emitting film 15.

Other aspects of this embodiment are the same as
15 those of the third embodiment and so are omitted.

To drive the electron-emitting device of this embodiment, the second electrode layer 14a and the second electrode layer 14b are connected to each other to have the same potential outside the electron-
20 emitting device.

The thus-manufactured electron-emitting device is driven under a condition where $V_a=10\text{kV}$, $V_b=0\text{V}$, and $D_1=2\text{mm}$. The electron emission performed in this case achieves an electron-emitting characteristic that is
25 almost the same as in the case of the electron-emitting device of the first embodiment.

<Sixth Embodiment>

Fig. 2 is a schematic plan view of the electron-emitting device manufactured in this embodiment, Fig. 12 is a schematic cross-sectional view of the electron-emitting device, and Figs. 13A to 13H show a method of manufacturing the electron-emitting device. In this embodiment, the first electrode 12 is stacked only in an area of the substrate 11 in which a convex portion composed of the insulating layer 13, the second electrode 14, and the electron-emitting film 15 is not formed. The method of manufacturing the electron-emitting device of this embodiment is described in detail below.

(Step 1)

First, as shown in Fig. 13A, the substrate 11 is prepared by sufficiently cleaning a quartz glass. Following this, with a sputtering method, the insulating layer 13 that is an SiO_2 film having a thickness of 300 nm and the second electrode 14 that is a Ta film having a thickness of 400 nm are stacked in this order onto the substrate 11.

(Step 2)

Next, as shown in Fig. 13B, a photomask pattern of a positive photoresist (AZ1500 manufactured by Clariant) is formed by spin coating, and is exposed to light and developed with a photolithography method to obtain a mask pattern 18. Then, as shown in Fig. 13C, dry etching is performed using CF_4 gas from above of the

mask pattern 18 functioning as a mask, so that the insulating layer 13 and the second electrode 14 are etched. This etching operation is terminated before the substrate 11 is also processed. Following this, as
5 shown in Fig. 13D, an Al film having a thickness of 200 nm is stacked as the first electrode 12.

(Step 3)

Next, the mask pattern 18 is peeled off. Then, as shown in Fig. 13E, a photomask pattern of a positive
10 photoresist (AZ1500 manufactured by Clariant) is formed by spin coating, and is exposed to light and developed with a photolithography method to obtain a mask pattern 19. Then, dry etching is performed using CF_4 gas from
15 above of the mask pattern 19 functioning as a mask, thereby obtaining a step-like shape of the second electrode 14 shown in Fig. 13F. The difference in height between the upper surface and the lower surface of the second electrode 14 is set to 300 nm, the
20 electrode length L1 is set at 100 μm , and the width of the lower surface is set to 0.5 μm .

(Step 4)

Following this, as shown in Fig. 13G, a diamond film having a thickness of 100 nm is stacked as the electron-emitting film 15 with a CVD method.

25 Finally, the mask pattern 19 used as a mask is completely removed to obtain the electron-emitting device of this embodiment shown in Fig. 13H.

The thus-manufactured electron-emitting device is driven under a condition where $V_a=10\text{kV}$, $V_b=0\text{V}$, and $D_1=2\text{ mm}$. The electron emission performed in this case achieves an electron-emitting characteristic that is almost the same as in the case of the electron-emitting device of the first embodiment.

<Seventh Embodiment>

The electron-emitting device of this embodiment has a construction where electron-emitting devices whose constructions are based on the first-sixth embodiments are arranged to oppose each other. In this embodiment, electron-emitting devices having a construction based on the first example are arranged to oppose each other. With this construction, the intensity of light emitted by a phosphor is increased.

Fig. 14 is a schematic cross-sectional view of the electron-emitting device of this embodiment, while Fig. 15 is a schematic plain view of the same.

The following description centers on the characteristic points of this embodiment and therefore the same points as in the aforementioned embodiments are omitted.

The electron-emitting device of this embodiment is manufactured in the same manner as in the first embodiment.

As to the size of the electron-emitting device, the thickness thereof is set at the same value as in

the first embodiment, although the hole diameter W2 shown in Fig. 15 is set at 84 μ m.

When the electron-emitting device of this embodiment is driven under a condition where $V_a=10$ kV, 5 $V_b=0$ V, and $D_1=2$ mm, electrons emitted from the electron-emitting film 15 gather at almost the center of the hole shown in Fig. 15 and the intensity of light emitted from the phosphor is remarkably increased.

<Eighth Embodiment>

10 In this embodiment, the electron-emitting device having the construction shown in Fig. 18A is manufactured. The following description concerns a method of manufacturing the electron-emitting device of this embodiment.

15 (Step 1)

The substrate 11 is prepared by sufficiently cleaning a quartz glass. Following this, with a sputtering method, the first electrode 12 that is an Ti layer having a thickness of 5 nm (not shown), the 20 insulating layer 13 that is an SiO_2 layer, and the second electrode 14 that is a Ti layer are stacked on the substrate 11 in this order.

Next, a resist pattern is formed using a positive photoresist (AZ1500 manufactured by Clariant) in a 25 photolithography step.

Then, dry etching is performed from above of the patterned photoresist functioning as a mask to obtain

the shapes of the first electrode 12, the insulating layer 13, and the second electrode 14 shown in Fig. 18A.

(Step 2)

5 Following this, a mask is formed to cover only a surface area of the second electrode in which the electron-emitting film 15 shown in Fig. 18A is not to be arranged.

(Step 3)

10 Next, a complex solution where isopropyl alcohol or the like is added to a Pd complex is applied to the surface area of the second electrode that is not covered with the mask.

15 After the application, heat treatment is performed in the air at 300°C to convert the applied complex solution into a palladium oxide film.

(Step 4)

20 The substrate is then heated to 200°C, the air is exhausted, and heat treatment is performed in a 2% hydrogen stream diluted by nitrogen. As a result of this step, a large number of Pd particles are formed on the surface of the second electrode 14.

(Step 5)

25 Following this, heat treatment is performed at 500°C for ten minutes in a 0.1% ethylene stream diluted by nitrogen to obtain the electron-emitting film 15. Then, the mask on the second electrode 14 is removed to

obtain the electron-emitting device of this embodiment.

By observing the electron-emitting film 15
manufactured in this example using a scanning electron
microscope, it is found that a large number of fibrous
5 carbons.

This device is placed in an vacuum apparatus and
the air inside the apparatus is sufficiently reduced to
a degree of vacuum of 1×10^{-5} Pa. Then, an anode voltage
 $V_a = 10$ KV is applied to the anode electrode 16 whose
10 distance H to the device is 2 mm, and a pulse voltage
of 15V is applied to the device as the driving voltage
 V_b . An electron emission current I_e is measured under
this condition.

The I_e characteristic of the electron-emitting
15 device of this example is such that I_e is dramatically
increased from around half of the applied voltage (V_b)
and, when $V_b = 15$ V, an electron emission current I_e of
around 1 pA is measured.

The beam obtained in this example has a shape
20 close to a rectangle that is long in the Y direction
and is short in the X direction. Also, a superfine
beam is obtained and the current I_e stays stable for a
long time period.

By observing the fibrous carbons of this electron-
25 emitting device using a transmission electron
microscope, it is found that the so-called graphite
nanofiber structure is obtained where graphenes are

laminated in the axial direction of each fiber as shown in the right area of Fig. 20.

<Ninth Embodiment>

5 An electron source and an image-forming apparatus are produced using the electron-emitting devices of the first-eighth examples.

10 The electron-emitting devices are arranged in a form of a 10 by 10 MTX. Wiring are connected in the manner shown in Fig. 6, where the X-directional wiring are connected to the second electrode layer and the Y-directional wiring are connected to the first electrode layer. The horizontal intervals and the vertical intervals between the devices are 150 μ m and 300 μ m, respectively. A phosphor is arranged over the devices so that a distance of 2 mm is maintained therebetween. 15 A voltage of 10kV is applied to the phosphor. In this manner, an image-forming apparatus and an electron source are achieved which are capable of performing matrix driving and high definition operations, having 20 uniform electron-emitting characteristics, and remaining stable for a long time period.

 As described above, the present invention realizes an electron-emitting device that has a uniform electron-emitting characteristic, emits an electron 25 beam whose diameter is small, has a simple construction, and is easy to be manufactured.

 Also, the first voltage applying means is used to

apply a certain voltage to an anode. As a result, if the electron-emitting device of the present invention is applied to an image-forming apparatus, an emission current is obtained through which has a phosphor emit
5 light having sufficient brightness.

Further, the electron-emitting device of the present invention realizes a high-performance electron source and image-forming apparatus.

WHAT IS CLAIMED IS:

1. An electron-emitting apparatus comprising:
an electron-emitting device including a first
electrode, a second electrode that is provided so as to
5 be insulated from the first electrode, and an electron-
emitting film connected to the second electrode; and
an anode provided at a predetermined distance from
the electron-emitting film,
wherein the first electrode, the second electrode,
10 and the electron-emitting film oppose the anode,
a distance between the anode and the electron-
emitting film is longer than a distance between the
anode and the second electrode, and
a distance between the anode and the first
15 electrode is longer than the distance between the anode
and the electron-emitting film.
2. An electron-emitting apparatus according to
Claim 1 further comprising a first voltage applying
20 means for applying, to the anode, a potential that is
higher than potentials applied to the first electrode
and the second electrode.
3. An electron-emitting apparatus according to
25 Claim 1 further comprising a second voltage applying
means for applying a voltage between the first
electrode and the second electrode.

4. An electron-emitting apparatus according to Claim 3,

wherein when electrons are emitted from the electron-emitting film, a potential applied to the first electrode is set so as to be at least equal to a potential applied to the second electrode.

5. An electron-emitting apparatus according to Claim 3,

wherein when no electrons are emitted from the electron-emitting film, a potential applied to the first electrode is set so as to be below a potential applied to the second electrode.

6. An electron-emitting apparatus according to Claim 1,

wherein the electron-emitting film includes carbon or a carbon compound.

7. An electron-emitting apparatus according to Claim 6,

wherein said carbon or said carbon compound includes at least one of diamond like carbon, graphite, diamond, a carbon nanotube, a graphitic nanofiber, and fullerene.

8. An electron source that is formed by arranging

a plurality of electron-emitting apparatuses of any one of claims 1 to 7 and emits electrons from at least one of the plurality of electron-emitting apparatuses according to an input signal.

5

9. An image-forming apparatus comprising:

the electron source of Claim 8; and

an image forming member on which an image is formed by irradiation with electrons emitted from the electron source.

10

10. An electron-emitting device comprising:

a first electrode arranged on a surface of a substrate;

15 an insulating layer arranged on the first electrode;

a second electrode arranged on the insulating layer; and

20 an electron-emitting film arranged on the second electrode,

whersin the second electrode has two side surfaces that oppose each other in a direction substantially parallel to the surface of the substrate, and the electron-emitting film is arranged so as to be shifted close to one of the two side surfaces.

25

11. An electron-emitting device according to

Claim 10,

wherein the electron-emitting film is an aggregate of fibers whose main ingredients are carbon.

5 12. An electron-emitting device according to Claim 11,

wherein each fiber whose main ingredient is carbon is one of a carbon nanotube and a graphite nanofiber.

10 13. An electron-emitting device according to Claim 11,

wherein each fiber whose main ingredient is carbon includes a graphene.

15 14. An electron-emitting device according to Claim 11,

wherein each fiber whose main ingredient is carbon includes a plurality of graphenes.

20 15. An electron-emitting device according to Claim 14,

wherein the plurality of graphenes are laminated in an axial direction of the fiber.

25 16. An electron-emitting device according to Claim 11,

wherein electrons are emitted from the electron-

emitting film when a potential applied to the first electrode is set so as to be at least equal to a potential applied to the second electrode.

5 17. An electron-emitting device according to Claim 11,

 wherein no electrons are emitted from the electron-emitting film when a potential applied to the first electrode is set so as to be below a potential
10 applied to the second electrode.

 18. An electron source in which are arranged a plurality of electron-emitting devices of any one of claims 11 to 17.

15

 19. An image-forming apparatus comprising:
 the electron source of Claim 18; and
 a phosphor.

ABSTRACT OF THE DISCLOSURE

Disclosed is an electron-emitting device, an electron source, and an image-forming apparatus that have uniform electron-emitting characteristics, emit
5 electron beams whose diameters are small, have simple constructions, and are easy to be manufactured. The electron-emitting device comprising: a first electrode arranged on a surface of a substrate; an insulating layer arranged on the first electrode; a second
10 electrode arranged on the insulating layer; and an electron-emitting film arranged on the second electrode, where the second electrode has two side surfaces that oppose each other in a direction parallel to the surface of the substrate, and the electron-
15 emitting film is arranged so as to be shifted toward one of the two side surfaces.

FIG. 1

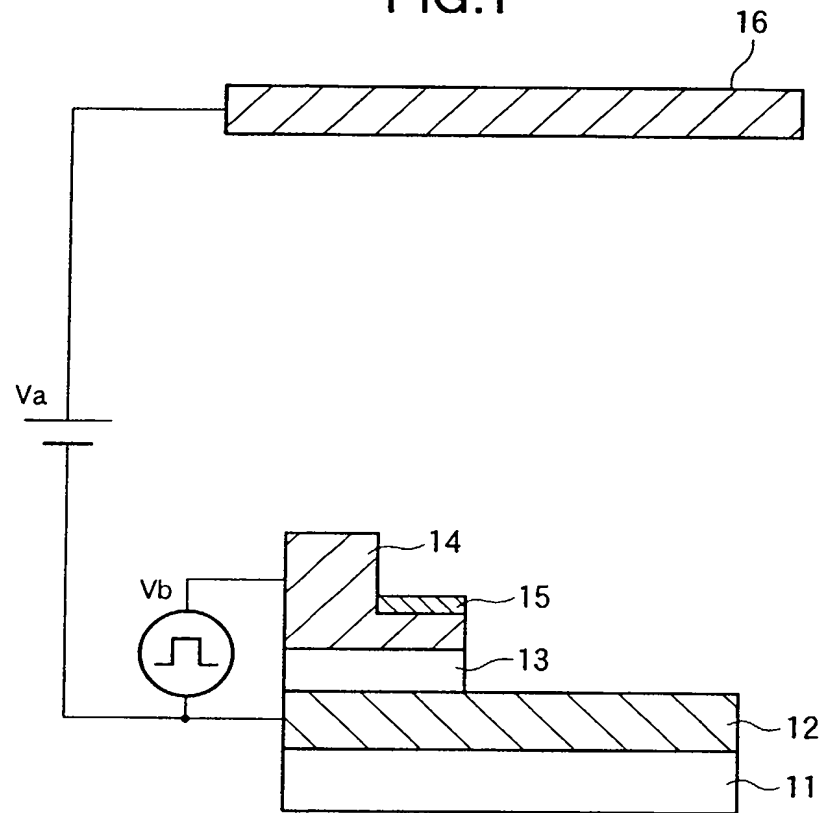


FIG.2

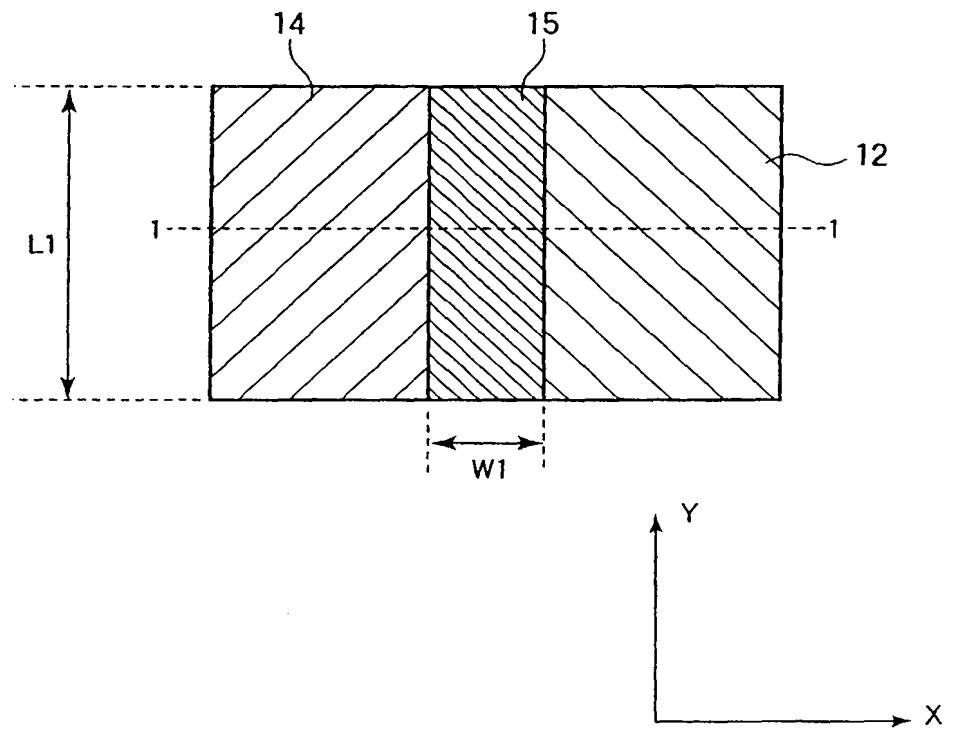


FIG.3

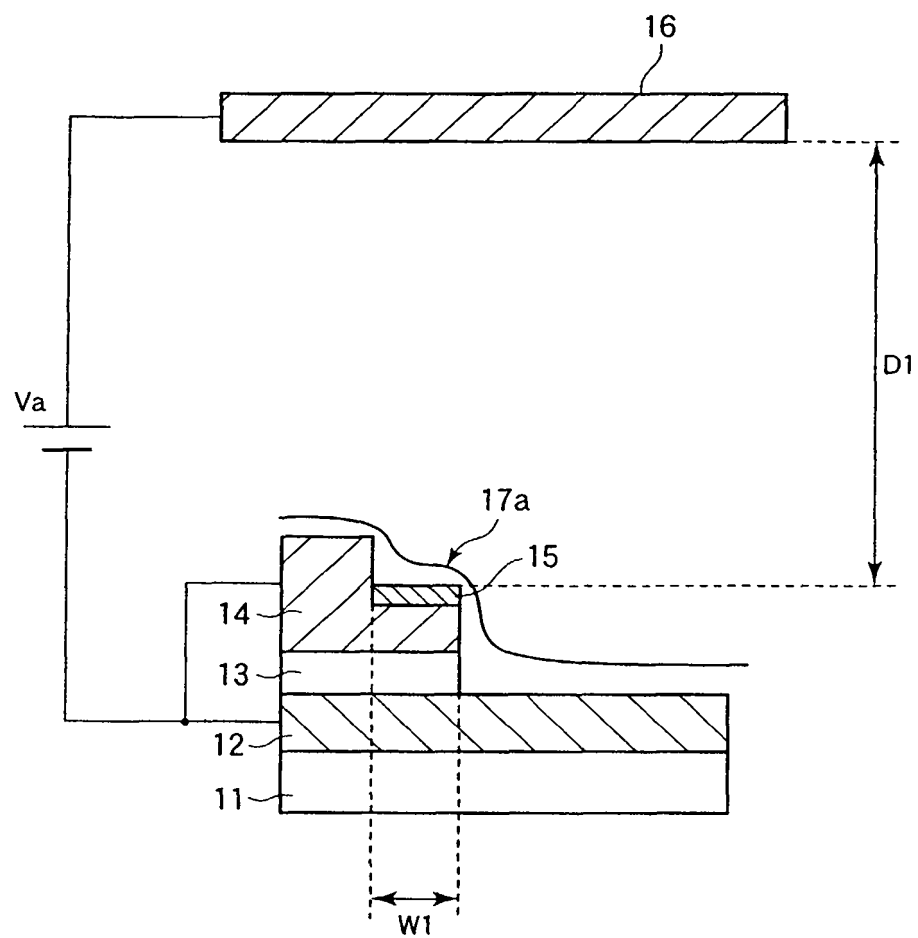


FIG. 4

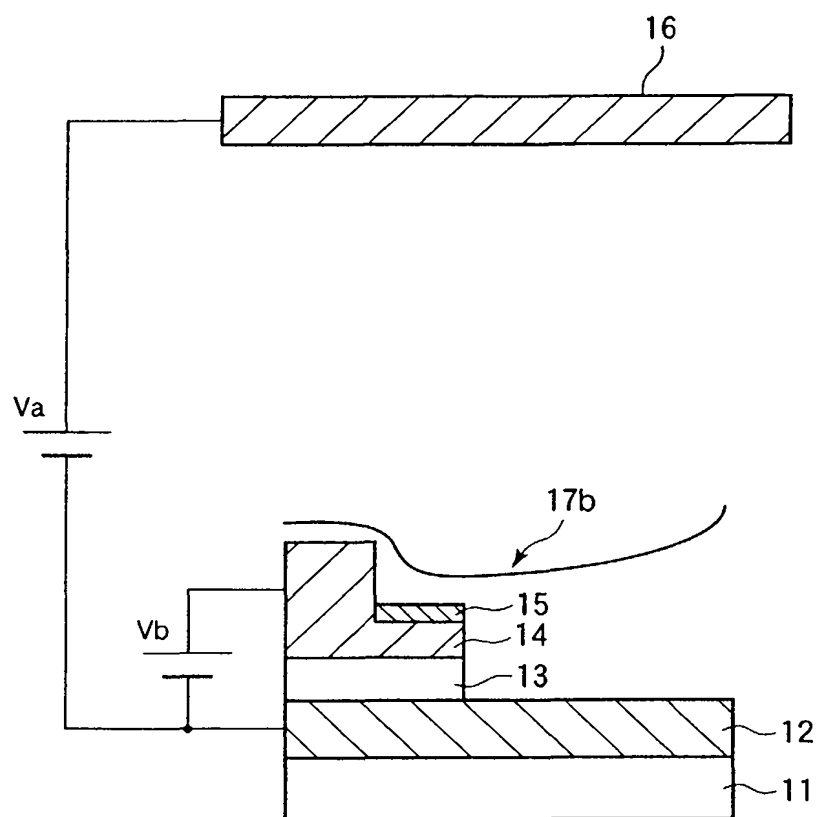


FIG.5A

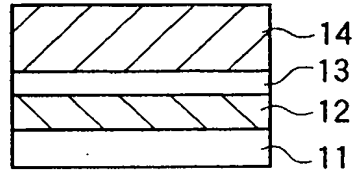


FIG.5B

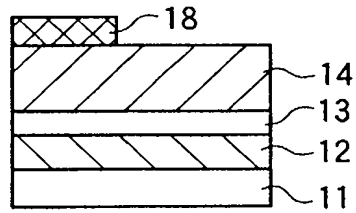


FIG.5C

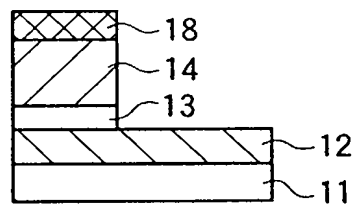


FIG.5D

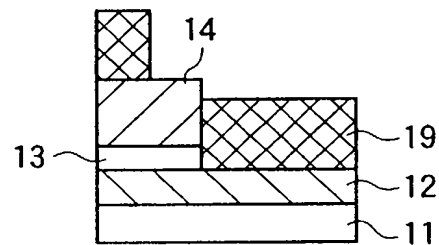


FIG.5E

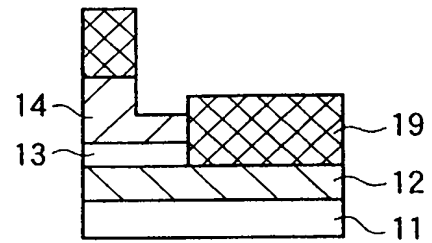


FIG.5F

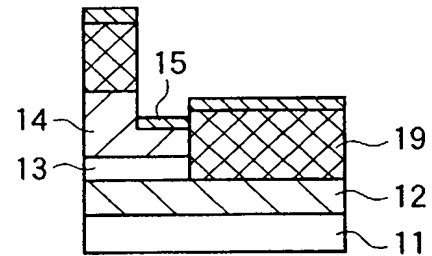


FIG.5G

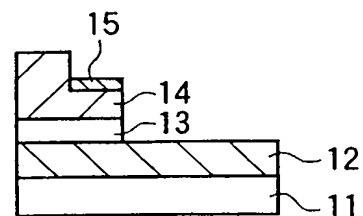


FIG.6

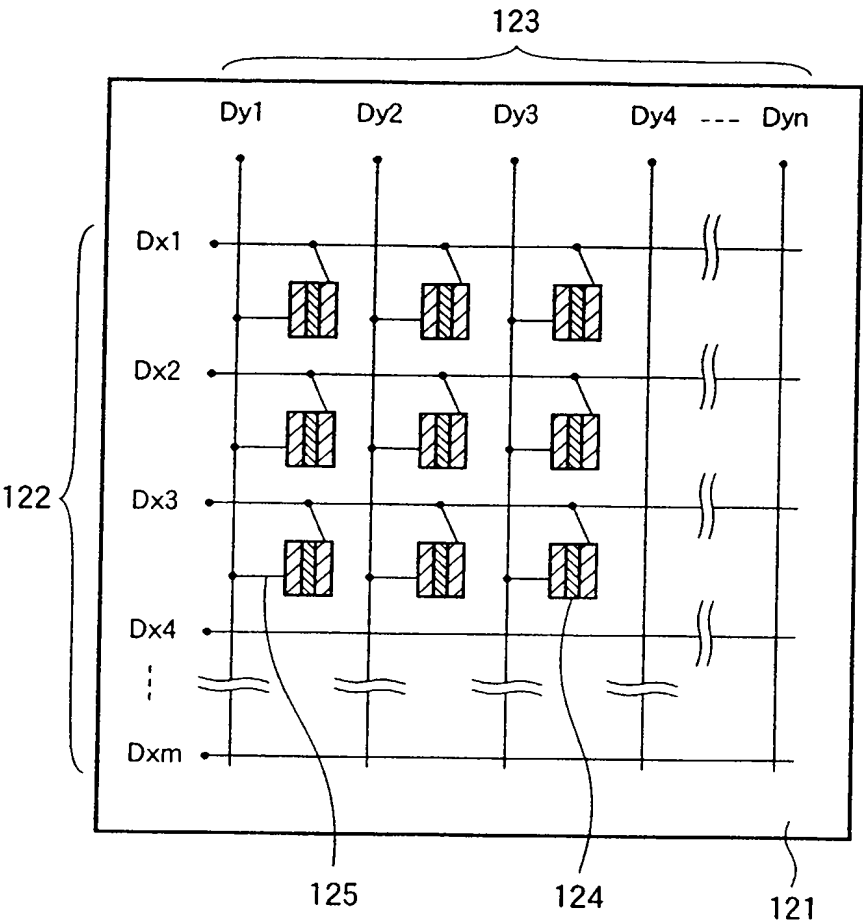


FIG.8A

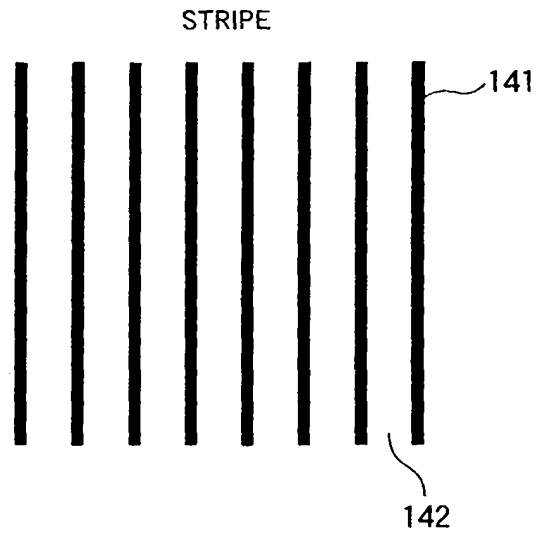


FIG.8B

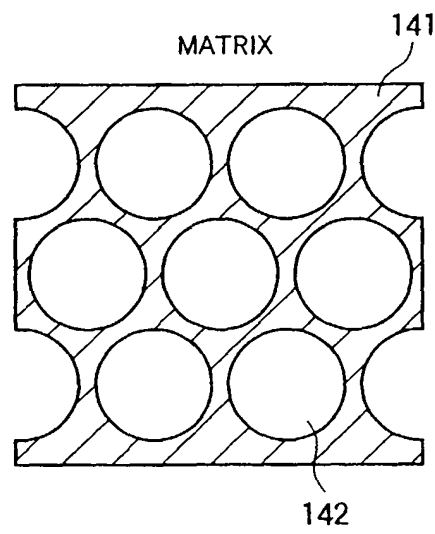


FIG.9

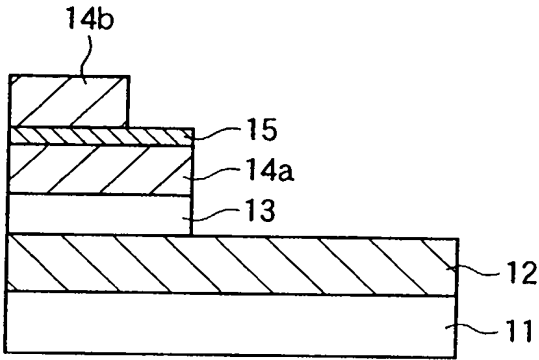


FIG.10A

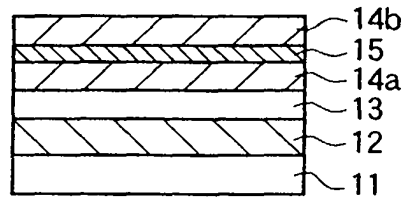


FIG.10B

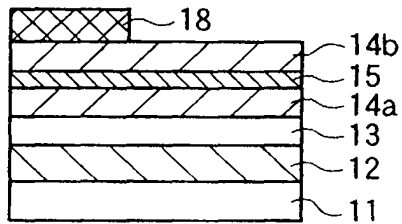


FIG.10C

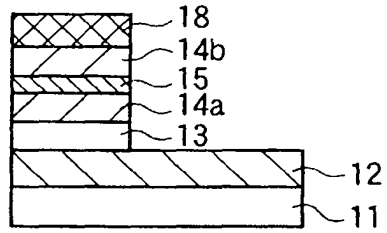


FIG.10D

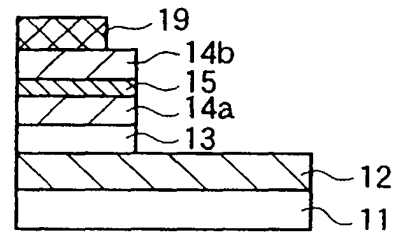


FIG.10E

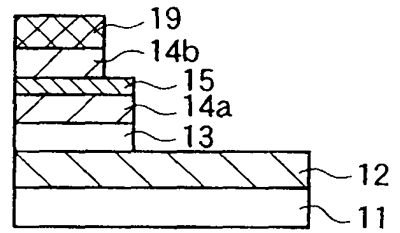


FIG.10F

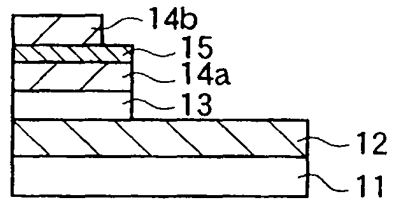


FIG.11

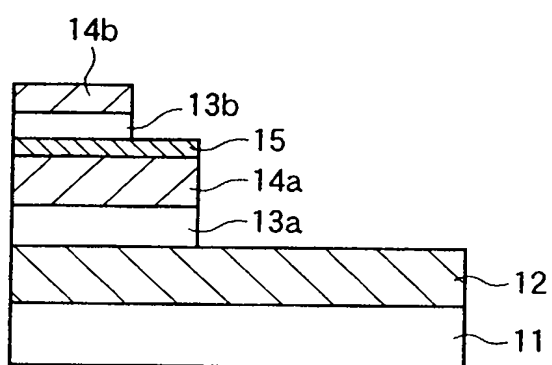


FIG.12

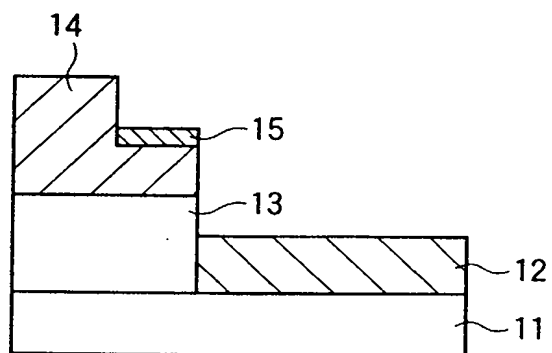


FIG.13A

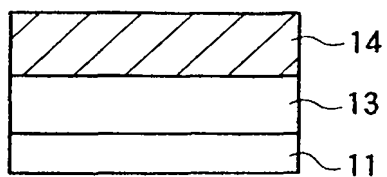


FIG.13B

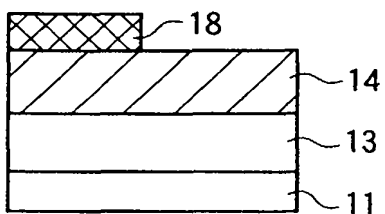


FIG.13C

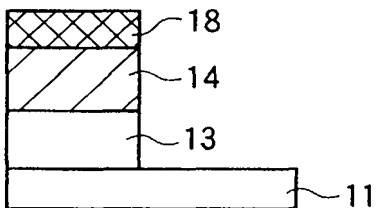


FIG.13D

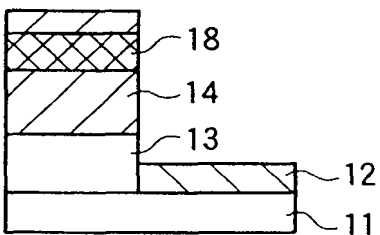


FIG.13E

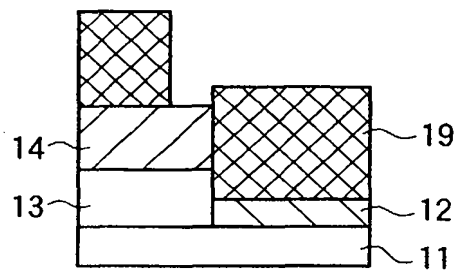


FIG.13F

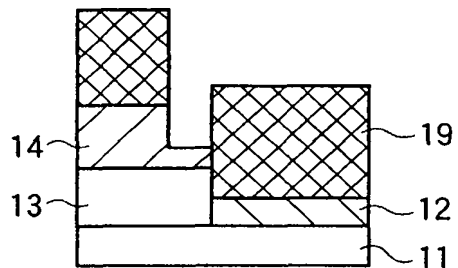


FIG.13G

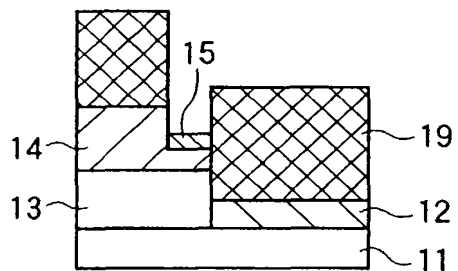


FIG.13H

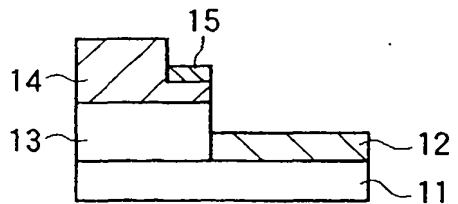


FIG.14

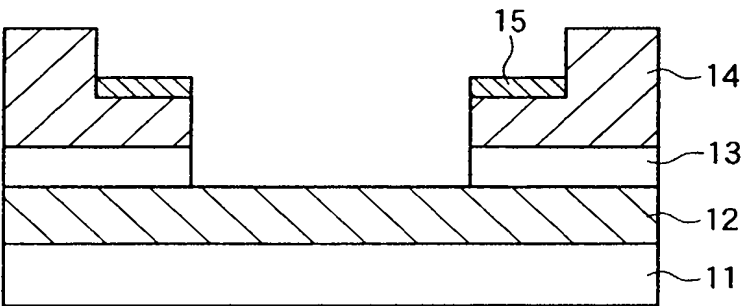


FIG.15

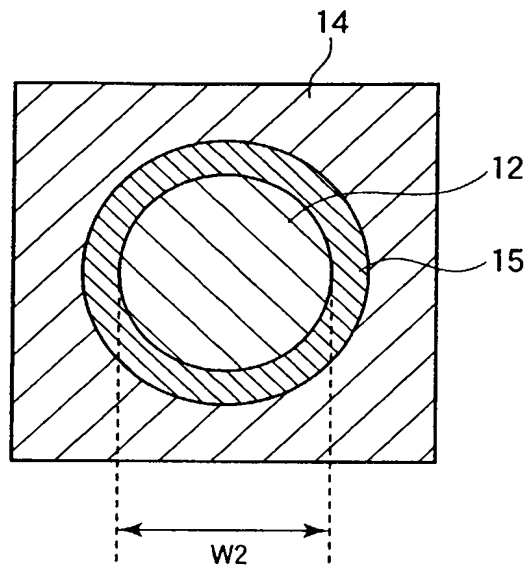


FIG.16

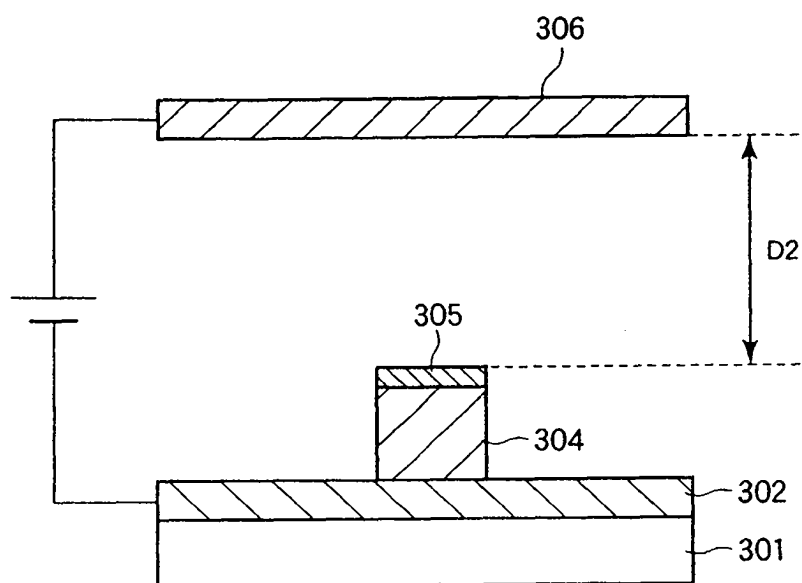


FIG.17

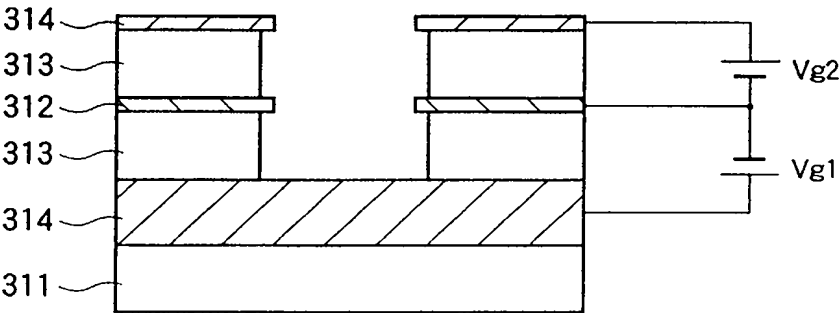


FIG.18A

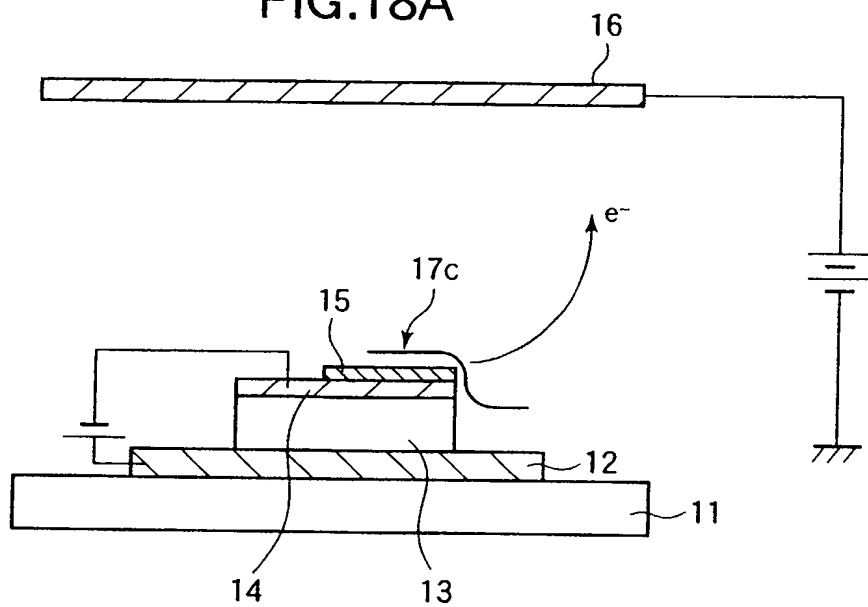


FIG.18B

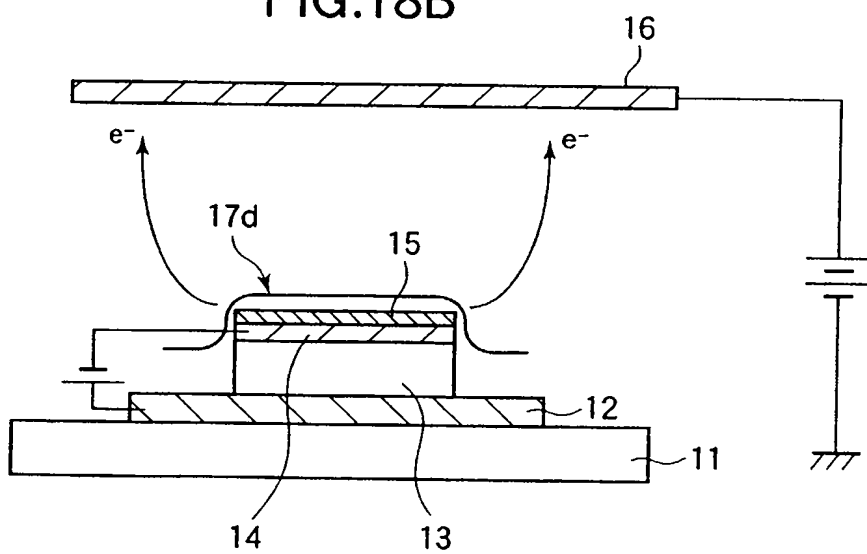


FIG.19

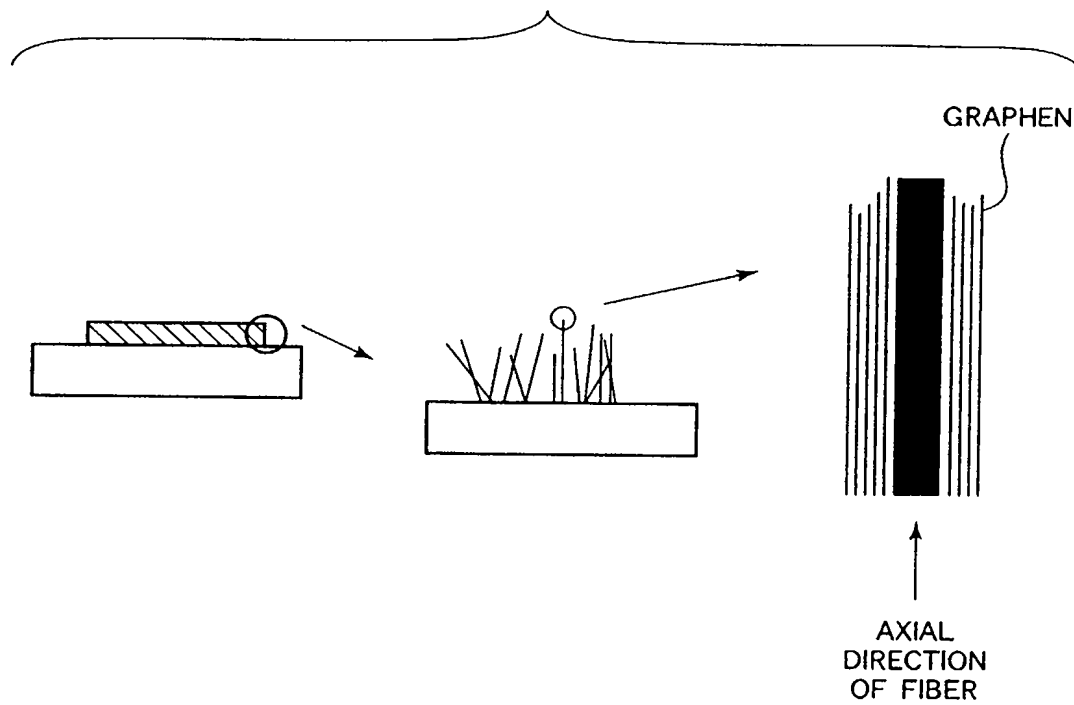
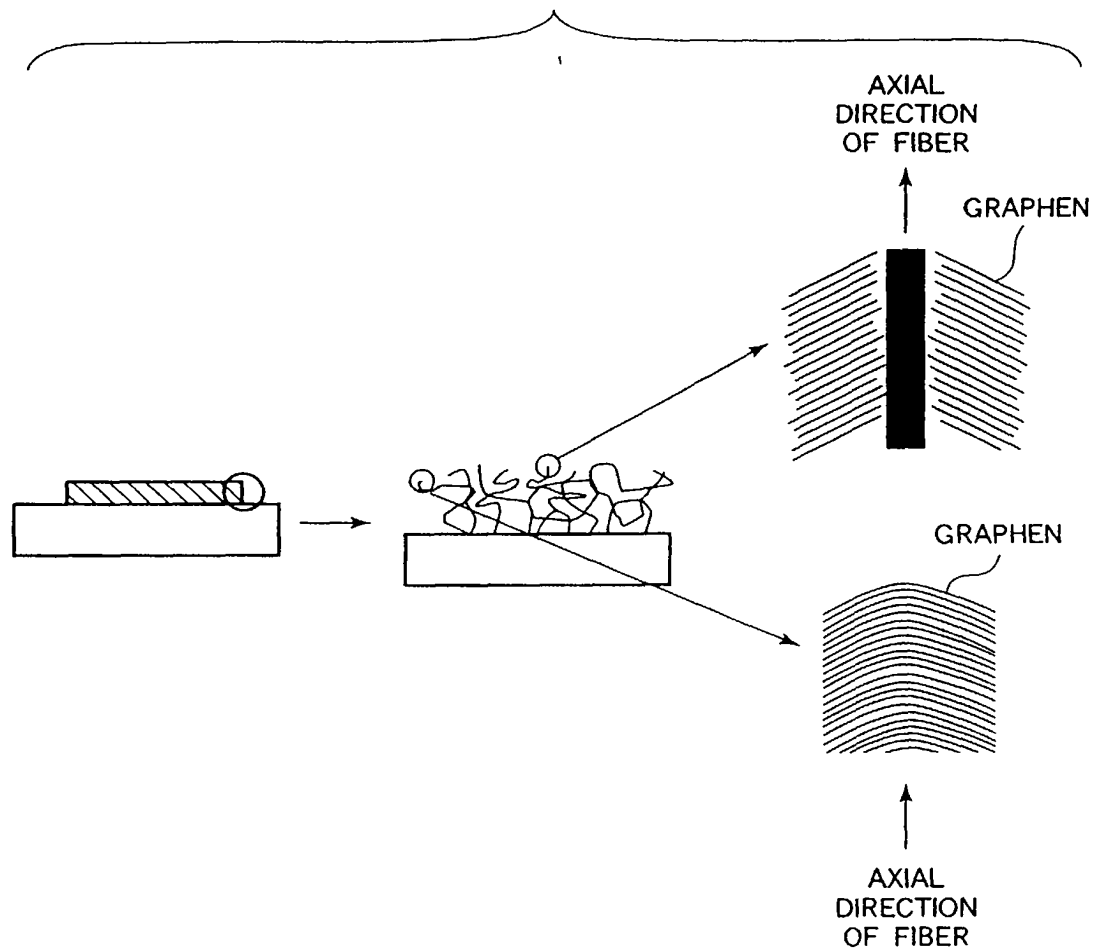


FIG.20



The attached application:

U.S. Application No.: 10/106,484

Filing Date: 3/27/02

Group Art Unit: 2879

is part of an IDS filed in U.S. Application N. : 09/341,585

- 1 -

CFO 16311 US
16/106,484
D/F: 3-27-02
GAC 2879

CATALYST USED TO FORM CARBON FIBER, METHOD OF MAKING
THE SAME AND ELECTRON EMITTING DEVICE,
ELECTRON SOURCE, IMAGE FORMING APPARATUS, SECONDARY
BATTERY AND BODY FOR STORING HYDROGEN

5

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to catalytic
material for promoting growth of carbon and its
10 preparing method, and electron emitting device,
electron source, image forming apparatus, secondary
battery and body for storing hydrogen using a carbon
fiber formed by the catalytic material. The image
forming apparatus of the present invention can be
15 used as an image forming apparatus for an optical
printer having a photosensitive drum as well as a
display device for television broadcasting, an image
display device of television conference system or
computer and so on.

20 Related Background Art

A method of making carbon fibril is disclosed
in Japanese Patent Laid-Open Gazette No. 4-504445
(corresponding family patents WO9007023 and
EP0451208). Further, a method of preparing
25 filamentary carbon is disclosed in Japanese Patent
Laid-Open No. 3-260119 (corresponding family patents
USP4900483 and EP433507).

Further, a method of preparing carbon nanotube is disclosed in Japan Patent Laid-Open No. 2000-95509.

An electron emitting element using carbon fiber is disclosed in USP4728851 publication, USP5872422
5 specification, USP5726524 specification, Japanese Patent Laid-Open No. 8-115652, Japanese Patent Laid-Open No. 2000-057934, Japanese Patent Laid-Open No. 2000-208028, Japanese Patent Laid-Open No. 2001-052598, "Carbon Nanotube FED with Graphite Nano-Fiber
10 Emitters" SID2000, pp398-401, "A nanotube-based field emission flat panel display" Applied Physics Letters, vol. 72, No. 22, pp2912-2913 (1998) and so on.

And, results of Raman spectrum analysis of carbon fiber is disclosed in Chemical Physics Letters
15 340 (2001), pp 413-418, as an example, as shown in Figs. 13A and 13B.

SUMMARY OF THE INVENTION

Generally in a conventional method of forming
20 carbon fiber such as carbon nanotube upon a substrate by using catalytic metal with the Plasma CVD manner, temperature of the substrate should be raised to 800 to 900°C, which may give an adverse effect on other members or increase costs.

25 An object of the present invention is to provide a catalyst, which enables to form carbon fiber satisfactorily at low temperature without

needing complex process, and its preparing method.

In addition, compared with so-called Spindt-type electron emitting element disclosed in such as C. A. Spindt, "Physical properties of thin-film field
5 emission cathodes with molybdenum cones", J. Applied. Physics, 47.5248 (1976), the electron emission element using the carbon fiber shows advantages of low electric field needed for electron emitting, low vacuum level needed for driving and furthermore high
10 emitted electron density.

However, in case of using the electron emitting element using carbon fiber as an electron source of a flat panel display, such characteristics should be maintained for a long time.

15 For example, if the emitting current density of the electron emitting element is greatly lowered in case of being applied to an image display device, this may cause serious deterioration of quality of display images. For that reason, improving the
20 characteristics further is one of essential problems in the electron emitting element using carbon fiber.

The present invention is related to such problems, and another object is to obtain electron emitting element, electron source and image forming
25 apparatus using carbon fiber, which may maintain advantages of low electric field needed for electron emitting, low vacuum level needed for driving and

furthermore high emitted current density for a long time.

As a result of comprehensive investigation for accomplish the above object, the inventors have found
5 that it is very preferable to use catalytic particles, which containing Pd and specific additives, as a catalyst used to form carbon fiber and then completed this invention.

According to one aspect of the present
10 invention, there is provided an electron emitting device comprising a film containing a plurality of carbon fibers, wherein the film, according to Raman spectrum characteristic detected by irradiating laser having a wavelength of 514.5nm, has a first peak of
15 intensity of Raman dispersion light in which Raman shift is in a range of $1355 \pm 10 \text{ kaiser}(\text{cm}^{-1})$ and a second peak of intensity of Raman scattering in which Raman shift is in a range of $1580 \pm 10 \text{ kaiser}$, and wherein a Full-Width Half-Maximum (FWHM2) of the
20 first peak and a Full-Width Half-Maximum (FWHM1) of the second peak satisfy a relation that $\text{FWHM2}/\text{FWHM1} \leq 1.2$.

According to another aspect of the present invention, there is provided an electron emitting
25 device comprising a film containing a plurality of carbon fibers, wherein the film, according to Raman spectrum characteristic detected by irradiating laser

having a wavelength of 514.5nm, has a first peak of intensity of Raman scattering in which Raman shift is in a range of $1355 \pm 10 \text{ kaiser}(\text{cm}^{-1})$ and a second peak of intensity of Raman scattering in which Raman shift is in a range of $1580 \pm 10 \text{ kaiser}$, and wherein a relative intensity h_2 , which is difference between background intensity and intensity of the Raman scattering at the first peak, and a relative intensity h_1 , which is difference between background intensity and intensity of the Raman scattering at the second peak, satisfy a relation that $1.3 \leq h_2/h_1$.

According to further aspect of the present invention, there is provided an electron emitting device comprising a film containing a plurality of carbon fibers, wherein the film, according to Raman spectrum characteristic detected by irradiating laser having a wavelength of 514.5nm, has a first peak of intensity of Raman scattering in which Raman shift is in a range of $1355 \pm 10 \text{ kaiser}(\text{cm}^{-1})$ and a second peak of intensity of Raman scattering in which Raman shift is in a range of $1580 \pm 10 \text{ kaiser}$, wherein a Full-Width Half-Maximum (FWHM2) of the first peak and a Full-Width Half-Maximum (FWHM1) of the second peak satisfy a relation that $\text{FWHM2}/\text{FWHM1} \leq 1.2$, and wherein a relative intensity h_2 , which is difference between background intensity and intensity of the Raman scattering at the first peak, and a relative

intensity h_1 , which is difference between background intensity and intensity of the Raman scattering at the second peak, satisfy a relation that $1.3 \leq h_2/h_1$.

According to still another aspect of the
5 present invention, there is provided features an electron emitting device comprising a film containing a plurality of carbon fibers, wherein the carbon fiber is graphite nanofiber having graphenes laminated not in parallel to the axial direction
10 thereof, and wherein the plurality of carbon fibers included in the film containing a plurality of carbon fibers have density over $10^3/\text{cm}^2$.

According to still another aspect of the present invention, there is provided an image display
15 device comprising a first substrate on which an electron emitting device having a film containing a plurality of carbon fibers is arranged, and a second substrate having a light emitting member and an anode electrode and arranged in opposition to the first
20 substrate, wherein the carbon fiber is graphite nanofiber having graphene laminated not in parallel to the axial direction thereof, wherein the number of electron emission sites of the film containing a plurality of carbon fibers is more than $10^3/\text{cm}$ when
25 electrons are emitted from the film containing a plurality of carbon fibers by electric field intensity more than $1 \times 10^5 \text{V/cm}$ is applied between

the film containing a plurality of carbon fiber and the anode electrode.

According to still another aspect of the present invention, there is provided a catalyst used
5 to form carbon fiber, which comprises Pd and at least one element selected from the group consisting of Fe, Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu, wherein 20atm% or more (atomic percentage) of the selected at least one element is contained to Pd.

10 According to still further aspect of the present invention there is provided a catalyst used to form carbon fiber comprises Pd and at least one element selected from the group consisting of Fe, Co and Ni, 20atm% or more (atomic percentage) of the
15 selected at least one element is contained to Pd.

According to still another aspect of the present invention there is provided a method of making a film containing a plurality of carbon fibers comprising the steps of: arranging a catalyst on a
20 substrate; and heat-treating the substrate on which the catalyst are arranged under circumstance including hydrocarbon gas and hydrogen, wherein the catalyst contains Pd and at least one element selected from the group consisting of Fe, Co, Ni, Y,
25 Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu, and 20 atm % or more (atomic percentage) of the selected at least one element is contained to Pd.

According to still another aspect of the present invention there is provided a method of making a film containing a plurality of carbon fibers comprising the steps of: arranging a plurality of
5 catalytic particles on a substrate; and heat-treating the substrate on which the plurality of catalytic particles are arranged under circumstance including hydrocarbon gas and hydrogen, wherein the catalyst contains Pd and at least one element selected from
10 the group consisting of Fe, Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu, and more than 20atm% (atomic percentage) of the selected at least one element is contained to Pd.

According to still another aspect of the
15 present invention, there is provided a method of making an electron emitting device comprising the steps of: disposing a film containing metal on a substrate; arranging a plurality of catalytic particles on the film containing metal; and heat-
20 treating the substrate on which the plurality of catalytic particles are arranged under circumstance including hydrocarbon gas and hydrogen to form a plurality of carbon fibers, wherein the catalytic particles contains Pd and at least one element
25 selected from the group consisting of Fe, Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu, and 20atm% or more (atomic percentage) of the

selected at least one element is contained to Pd.

According to still another aspect of the present invention, there is provided a method of making an electron emitting device comprising the

5 steps of: disposing a film containing metal on a substrate; arranging a plurality of catalytic particles on the substrate containing metal; and heat-treating the substrate on which the plurality of catalytic particles are arranged under circumstance

10 including hydrocarbon gas and hydrogen to form a plurality of carbon fibers, wherein the catalytic particles contains Pd and at least one element selected from the group consisting of Fe, Co and Ni, and more than 20atm% (atomic percentage) of the

15 selected at least one element is contained to Pd.

According to still another aspect of the present invention, there is provided a cathode of a secondary battery containing a plurality of carbon fibers, wherein a film containing a plurality of the

20 carbon fibers, according to Raman spectrum characteristic detected by irradiating laser having a wavelength of 514.5nm, has a first peak of intensity of Raman scattering in which Raman shift is in a range of $1355 \pm 10 \text{ kaiser}(\text{cm}^{-1})$ and a second peak of

25 intensity of Raman scattering in which Raman shift is in a range of $1580 \pm 10 \text{ kaiser}$, and wherein a Full-Width Half-Maximum (FWHM2) of the first peak and a

Full-Width Half-Maximum (FWHM1) of the second peak satisfy a relation that $FWHM2/FWHM1 \leq 1.2$.

According to still another aspect of the present invention, there is provided a cathode of a secondary battery containing a plurality of carbon fibers, wherein a film containing a plurality of the carbon fibers, according to Raman spectrum characteristic detected by irradiating laser having a wavelength of 514.5nm, has a first peak of intensity of Raman scattering in which Raman shift is in a range of $1355 \pm 10 \text{ kaiser}(\text{cm}^{-1})$ and a second peak of intensity of Raman scattering in which Raman shift is in a range of $1580 \pm 10 \text{ kaiser}$, and wherein a relative intensity h_2 , which is difference between background intensity and intensity of the Raman scattering at the first peak, and a relative intensity h_1 , which is difference between background intensity and intensity of the Raman scattering at the second peak, satisfy a relation that $1.3 \leq h_2/h_1$.

According to still another aspect of the present invention, there is provided a cathode of a secondary battery containing a plurality of carbon fibers, wherein the plurality of carbon fibers, according to Raman spectrum characteristic detected by irradiating laser having a wavelength of 514.5nm, has a first peak of intensity of Raman scattering in which Raman shift is in a range of $1355 \pm$

10kaiser(cm^{-1}) and a second peak of intensity of Raman scattering in which Raman shift is in a range of $1580 \pm 10\text{kaiser}$, wherein a Full-Width Half-Maximum (FWHM2) of the first peak and a Full-Width Half-Maximum (FWHM1) of the second peak satisfy a relation that $\text{FWHM2}/\text{FWHM1} \leq 1.2$, and wherein a relative intensity h_2 , which is difference between background intensity and intensity of the Raman scattering at the first peak, and a relative intensity h_1 , which is difference between background intensity and intensity of the Raman scattering at the second peak, satisfy a relation that $1.3 \leq h_2/h_1$.

According to still another aspect of the present invention, there is provided a body for a hydrogen storing, containing a plurality of carbon fibers, wherein the plurality of carbon fibers, according to Raman spectrum characteristic detected by irradiating laser having a wavelength of 514.5nm, has a first peak of intensity of Raman scattering in which Raman shift is in a range of $1355 \pm 10\text{kaiser}(\text{cm}^{-1})$ and a second peak of intensity of Raman scattering in which Raman shift is in a range of $1580 \pm 10\text{kaiser}$, and wherein a Full-Width Half-Maximum (FWHM2) of the first peak and a Full-Width Half-Maximum (FWHM1) of the second peak satisfy a relation that $\text{FWHM2}/\text{FWHM1} \leq 1.2$.

According to still another aspect of the

present invention, there is provided a body for a hydrogen storing, containing a plurality of carbon fibers, wherein the plurality of carbon fibers, according to Raman spectrum characteristic detected
5 by irradiating laser having a wavelength of 514.5nm, has a first peak of intensity of Raman scattering in which Raman shift is in a range of $1355 \pm 10\text{kaiser}(\text{cm}^{-1})$ and a second peak of intensity of Raman scattering in which Raman shift is in a range of
10 $1580 \pm 10\text{kaiser}$, and wherein a relative intensity h_2 , which is difference between background intensity and intensity of the Raman scattering at the first peak, and a relative intensity h_1 , which is difference between background intensity and intensity of the
15 Raman scattering at the second peak, satisfy a relation that $1.3 \leq h_2/h_1$.

According to still another aspect of the present invention, there is provided a body for a hydrogen storing, containing a plurality of carbon
20 fibers, wherein the plurality of carbon fibers, according to Raman spectrum characteristic detected by irradiating laser having a wavelength of 514.5nm, has a first peak of intensity of Raman scattering in which Raman shift is in a range of $1355 \pm$
25 $10\text{kaiser}(\text{cm}^{-1})$ and a second peak of intensity of Raman scattering in which Raman shift is in a range of $1580 \pm 10\text{kaiser}$, wherein a Full-Width Half-Maximum

(FWHM2) of the first peak and a Full-Width Half-Maximum (FWHM1) of the second peak satisfy a relation that $FWHM2/FWHM1 \leq 1.2$, and

wherein a relative intensity h_2 , which is
5 difference between background intensity and intensity of the Raman scattering at the first peak, and a relative intensity h_1 , which is difference between background intensity and intensity of the Raman scattering at the second peak, satisfy a relation
10 that $1.3 \leq h_2/h_1$.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A, 1B, 1C, 1D and 1E show examples of the process of making electron emitting elements
15 using catalytic particles of the present invention.

Figs. 2A and 2B are plane view and sectional view showing an example of the electron emitting element using the catalytic particles of the present invention.

20 Fig. 3 is a diagram for illustrating operation when driving the electron emitting element of the present invention.

Fig. 4 is a graph illustrating basic operational characteristics of the electron emitting
25 element of the present invention.

Fig. 5 shows an example of a passive matrix circuit using a plurality of electron sources of the

present invention.

Fig. 6 shows an example of an image forming panel using the electron source of the present invention.

5 Fig. 7 is a schematic diagram showing configuration of a carbon nanotube.

Fig. 8 is a schematic diagram showing configuration of a graphite nanofiber.

10 Fig. 9 is a graph showing characteristics of the electron emitting element of the present invention.

Fig. 10 is a graph showing Raman Spectra of the electron emitting element of the present invention.

15 Fig. 11 is a graph showing Raman Spectra of the electron emitting element of the present invention.

Fig. 12 is a graph showing Raman Spectra and aging of the electron emitting element of the present invention.

20 Fig. 13 is a graph showing Raman Spectra of conventional carbon fiber.

Fig. 14 is a schematic diagram showing configuration of the electron emitting element of the present invention.

25 Fig. 15 is a schematic diagram showing configuration of the electron emitting element of the present invention.

Figs. 16A, 16B and 16C are schematic diagrams

showing configuration of Graphite nanofiber.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

An embodiment of catalyst and method of making
5 the catalyst, carbon fiber formed using the catalyst,
and electron emitting device, cathode of a secondary
battery, body for hydrogen storing, electron source
and image forming apparatus using a carbon fiber
according to the present invention is described in
10 detail. But, size, material, shape and relative
position of units described below do not limit the
scope of the invention, if not mentioning specific
limitation. The making process described below is
also not unique.

15 First of all, the catalyst of the present
invention is explained.

The catalyst of the present invention
particularly contains Pd used for growth of carbon
fiber (promoting growth of carbon fiber), and at
20 least one element of Fe, Co, Ni, Y, Rh, Pt, La, Ce,
Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu is added to the
catalyst. And, in case of being used to form carbon
fiber, the catalyst is preferable and important in
the viewpoint that it controls shape such as diameter
25 of the carbon fiber of a particle state.

Among the elements added in combination with Pd,
it is preferred that at least any of Fe, Ni and Co is

added, and combination of Pd and Co is more preferable. If the carbon fiber is made using catalytic particles containing Pd and any selected element among Fe, Ni and Co and applied the obtained
5 carbon fiber to an electron emitting device, it is possible to obtain very excellent applied voltage-electron emission current characteristics. At the same time, it is also possible to obtain stable electron emitting characteristic for a long time. In
10 addition, it is also preferred that the added element (Fe, Ni or Co) composes the catalytic particles in an alloy state with Pd to make a plurality of carbon fibers stably with high uniformity.

At this time, the term "carbon fiber" in the
15 present invention means fiber containing carbon as a main component or carbon in state of fiber. And, "carbon fiber" of the present invention includes carbon nanotube, graphite nanofiber, amorphous carbon fiber and diamond fiber. And, as described later, in
20 the electron emitting device of the present invention, graphite nanofiber is preferably used among the carbon fibers in aspect of its electron emission characteristic.

The reason that Pd is used as a component in
25 the present invention is as followed.

Though other catalysts except Pd become oxide by reaction with moisture and oxygen in atmosphere as

soon as they are exposed to the atmosphere, Pd catalyst maintains metallic combining state more stably rather than other catalysts.

Particularly, the metallic catalytic particles
5 in Fe group have danger of explosion due to abrupt chemical reaction when being exposed to the atmosphere, while the metallic Pd catalyst does not have such danger. And, metallic catalysts containing Co, Ni, Fe or the like added to Pd progress oxidation
10 reaction slowly, so enabling to treat the catalyst safely.

On the other hand, Pd shows a unique behavior related to nature of easily receiving hydrogen in the catalyst. If exposing Pd to deoxidization
15 circumstance of such as hydrogen or organic gas, particles containing hydrogen are combined each other at a relatively low temperature (more than about 450°C) to be particles having bigger shape than that of an initial state. Owing to such phenomenon, there
20 are caused some problems for Pd particles changing into bigger shape in the facts that growth temperature of carbon fiber is raised and threshold of electron emission is increased.

To avoid such problems, there is a method of
25 not exposing the catalyst to hydrogen or hydrocarbon until reaching at a temperature required for growth of carbon fiber, but there is found more effective

method that prevent deformation to be larger particle by adding at least one of Fe, Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu (preferably Fe, Co or Ni) into Pd particles to be combined each other.

5 The above result is remarkable when a ratio of the added element to Pd is more than 5atm% (atomic percentage). And, if the ratio (atomic percentage) of the added element to Pd exceeds 80atm%, it tends to require deoxidization process such as active hydrogen
10 addition or gets into a slow growth of the carbon fiber. In addition, if the ratio (atomic ratio) of the added element to Pd exceeds 80atm%, crystal structure of the formed carbon fiber tends to be extremely changed since the catalyst has
15 characteristics similar to the catalyst having 100% of added element. For that reason, the added element to Pd is preferably less than 80atm%.

And, the catalyst of the present invention is preferably in a particle state in aspect of forming
20 carbon fiber.

Furthermore, though described in detail later, when applying carbon fiber to the electron emitting device, one in which carbon fibers are arranged in high density (called as "film containing a plurality
25 of carbon fibers") is applied to one electron emitting device. When forming such a film containing a plurality of carbon fibers with high uniformity and

stability, it is essential that the element added to Pd contained in the catalytic particles of the present invention is an alloy state.

The present invention, though described in
5 detail later, is to form a minute nucleus (catalyst particle (with a diameter of 1 to 100nm)) with the above catalytic materials to thereby grow carbon fiber preferably applied to the electron emitting device through the nucleus (catalyst particle) by
10 pyrolysis of hydrocarbon gas using the thermal CVD manner. At this time, there are used, for example, acetylene, ethylene, methane, propane, propylene and so on for the hydrocarbon gas. In addition, steam of organic agents such as ethanol and acetone are often
15 used.

Figs. 7, 8, 16A, 16B and 16C exemplarily show schematic diagrams of the film containing a plurality of carbon fibers obtained by decomposition of hydrocarbon gas using the catalyst particles of the
20 present invention. In each figure, a shape of carbon fiber seen at an optical microscope level (~1000 times) are schematically shown to left, a shape at an scanning electron microscope (SEM) level (~30,000 times) to center, and a shape at a transmission
25 electron microscope (TEM) level (~1,000,000 times) to right.

As shown in Fig. 7, if graphene is in a

cylindrical shape, it is called as carbon nanotube
(if multi-layered cylindrical shape, it called as
multi-wall nanotube), and the threshold required for
electron emission is lowest when an end of the tube
5 is open.

Graphite nanofiber is schematically shown in
Figs. 8, 16A, 16B and 16C. This type of carbon fiber
is composed as a multi-layered graphene. More
specifically, as shown in the right schematic figure
10 of Fig. 8, graphite nanofiber designates fiber-state
material in which graphenes 23 are laminated to a
longitudinal direction (fiber axis direction). Or,
as shown in the right schematic figure of Fig. 8, it
designates the fiber-state materials in which the
15 graphenes 23 are arranged not parallel to the fiber
axis. Even though the graphene 23 is substantially
perpendicular to the axis of fiber, it is included in
graphite nanofiber in the present invention.

In addition, the first crossed surface of
20 graphite is called as "graphene" or "graphenesheet".
More specifically, graphite is made by laminating
carbon planes, which is formed by the covalent bond
of carbon atoms by sp^2 hybridization (trigonal
hybridization) and arranged as if regular hexagons
25 are laid, with maintaining a distance ideally of
3.354Å. This carbon plane is called as "graphene" or
"graphenesheet".

In case the above carbon fiber is used as electron emitting device, the threshold of this electron emission is about 1V to 10V/ μm , which is preferably as the electron emitting materials.

5 And, in case of forming the electron emitting device using carbon fiber, the film containing a plurality of carbon fibers are used for one electron emitting device. However, when such a film containing a plurality of carbon fiber is used,
10 graphite nanofiber is preferably used as carbon fiber. It is because the electron emitting device in which the film containing a plurality of graphite nanofibers is used as an electron emitting film may obtain greater electron emission current density
15 rather than the case of using carbon nanotube.

In addition, when the electron emitting device is used as, for example, a display and an electron source, it is required to maintain the good electron emission characteristic for a long time. As a result
20 of investigation conducted by the inventors, it has been found that it is possible to maintain the good electron emission characteristic of the electron emitting device using the film containing a plurality of carbon fibers if Raman spectrum analysis of the
25 film gives a specific result.

Fig. 11 shows characteristics remarkably appeared in the film containing a plurality of carbon

fibers in which the film may maintain the good electron emission characteristic for a long time. Specifically, it schematically shows intensity distribution characteristic (Raman Spectra) of Raman scattering (scattered light) detected when irradiating laser with a wavelength of 514.5nm to the film containing a plurality of carbon fibers of the present invention. In addition, in Fig. 11, a horizontal axis designates deviation extent (called as "Raman Shift") of frequency of Raman scattering from Rayleigh scattering, while a vertical axis designates intensity of Raman scattering .

As shown in Fig. 11, the film containing a plurality of carbon fibers of the present invention shows a clear peak ("first peak") of Raman scattering intensity when Raman shift is in range of $1355 \pm 10 \text{ kaiser}(\text{cm}^{-1})$, and a clear peak ("second peak") of Raman scattering intensity when Raman shift is in range of $1580 \pm 10 \text{ kaiser}(\text{cm}^{-1})$. It's believed that the first peak may be corresponded to so-called "D band", while the second peak may be corresponded to so-called "G band".

And, the film containing a plurality of carbon fibers of the present invention, as shown in Fig. 11, has a relative intensity I_2 , which is a difference between Raman scattering intensity of the first peak and background intensity (baseline), at least 1.3

times of a relative intensity h_1 , which is a difference between Raman scattering intensity of the second peak and background intensity. And more preferably, in the film containing a plurality of
5 carbon fibers of the present invention, a relative intensity h_2 , which is a difference between Raman scattering intensity of the first peak and background intensity (baseline), is 1.3 times or more and 2.5 times or lower of a relative intensity h_1 ,
10 which is a difference between Raman scattering intensity of the second peak and background intensity.

In addition, in this invention, the background intensity designates one connecting Raman scattering intensity at 1100 cm^{-1} and Raman scattering intensity
15 at 1700 cm^{-1} in a straight line in an averaged result of an actual measured Raman spectrum graph.

And, the film containing a plurality of carbon fibers of the present invention satisfies the relation between Full-Width Half-Maximum of the first
20 peak FWHM2 and Full-Width Half-Maximum of the second peak FWHM1 that $\text{FWHM2}/\text{FWHM1} \leq 1.2$.

And preferably, the film containing a plurality of carbon fibers of the present invention satisfies the relation between Full-Width Half-Maximum of the
25 first peak FWHM2 and Full-Width Half-Maximum of the second peak FWHM1 that $\text{FWHM2}/\text{FWHM1} \leq 1.2$, and has a relative intensity h_2 , which is a difference between

Raman scattering intensity of the first peak and background intensity (baseline), at least 1.3 times of a relative intensity h_1 , which is a difference between Raman scattering intensity of the second peak and background intensity. And more preferably, the film containing a plurality of carbon fibers of the present invention satisfies the relation between Full-Width Half-Maximum of the first peak FWHM2 and Full-Width Half-Maximum of the second peak FWHM1 that $FWHM2/FWHM1 \leq 1.2$, and a relative intensity h_2 , which is a difference between Raman scattering intensity of the first peak and background intensity (baseline), is 1.3 times or more and 2.5 times or lower of a relative intensity h_1 , which is a difference between Raman scattering intensity of the second peak and background intensity.

More preferably, the film containing a plurality of carbon fibers of the present invention has a relative intensity h_3 , which is a difference between a minimum intensity between the first peak and the second peak (or between D band and G band) of Raman scattering intensity and the background intensity, 1/10 or lower of a relative intensity h_2 , which is a difference between a minimum intensity of Raman scattering intensity having the first peak, in addition to each of the above characteristics (the Full-Width Half-Maximum of the first peak and the

second peak and/or the intensity ratio between the first peak and the second peak). And, more preferably, the relative intensity h_3 is $1/15$ or lower of the relative intensity h_2 .

5 As described above, by the fact that the minimum intensity h_3 of Raman scattering intensity is $1/10$ or lower, particularly $1/15$ or lower, of Raman scattering intensity having the first peak in relation of the first peak and the second peak (or D
10 band and G band), crystallization of the carbon fiber is improved and thus it is possible to maintain the good electron emission characteristic for a long time.

 The electron emitting device using the film containing a plurality of carbon fibers of the
15 present invention satisfying the above conditions has greater initial electron emission current density, as described below, or lower deterioration of the electron emission characteristic with time, and may become an electron emitting device with good life
20 characteristic. Though the reason that the good life characteristic is obtained for a long time is not clear, it is judged in the present invention that the relation with h_3 is also one of important factors in addition to the relation between h_1 and h_2 and the
25 relation between FWHM1 and FWHM2. In addition, the relation between h_2 and h_3 gives a stability of electron emitting characteristic.

Now, an example of methods for making the film containing a plurality of carbon fibers is described. But, size, material, shape, relative position, used gas and chemicals of units described below are just
5 one example, but not intended to limit the scope of the present invention.

The film containing a plurality of carbon fibers with the above Raman shift characteristics can be obtained by growing carbon fibers through the
10 below-described catalytic particles of the present invention (particularly, particles comprising Pd and Co alloy or particles comprising Pd and Ni alloy).

The electron emitting device using particularly graphite nanofiber among carbon fibers made using the
15 catalytic particles of the present invention is not limited to device configuration shown in Fig. 2 described later, and may generate electron emission at a low electric field, and be able to obtain large emitting currents, and be easily manufactured, and
20 have stable electron emission characteristics.

Graphite nanofiber, differently to carbon nanotube and so on, has fine convex and concave protrusions on a surface (a side of fiber) as shown in Fig. 8 or the like, so thus it is thought that
25 electric field concentration may be easily appeared and the electron will be easily emitted. And, it is also considered that the electron emission would be

easier since graphene has an extended shape from a central axis of the fiber toward outside (surface) of the fiber. One carbon nanutube is chemically inert since the side of fiber is basically corresponding to
5 (002)plane of graphite and does not have protrusion like the graphite nanofiber, so it could be thought that electron emission is not easy at the side of fiber. For that reason, graphite nanofiber among carbon fibers is considered preferable for the
10 electron emitting device.

For example, it is possible to set the film containing a plurality of graphite nanofiber as an emitter and then make an electron emitting device by providing electrode (gate electrode) for controlling
15 electron emission from this emitter. Then, by arranging a light emitting member, which emits light by irradiation of electrons emitted from the graphite nanofiber, on a trajectory of the electrons, a light emitting device such as lamp may be formed. In
20 addition, it is also possible to configure an image display device such as display by arranging a plurality of electron emitting devices using the film containing a plurality of graphite nanofibers as well as preparing anode electrode having a light emitting
25 member such as fluorescent substance. The electron emitting device, light emitting device or image display device using the graphite nanofiber of the

present invention may stably emit electrons without maintaining inner in an ultra-high-vacuum state as the conventional electron emitting device does, and since they emits electrons at a lower electric field, very reliable devices may be manufactured very conveniently.

And, particularly, when arranging a plurality of catalytic particles of the present invention and then applying the electric field intensity of $1 \times 10^5 \text{V/cm}$ between the anode electrode and the film containing a plurality of graphite nanofiber grown from the catalytic particles, a density of 10^3number/cm^2 can be obtained at electron emission site.

As an example of the methods of making the catalyst (particularly, particulate catalyst) of the present invention, there is vacuum coevaporation, and specifically it is possible to make the catalyst by using Pd as a first evaporation source of the vacuum evaporation and at least one element selected in the group consisting of Fe, Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu as a second evaporation source of the vacuum evaporation.

As for the vapor evaporation, there may be used electron beam evaporation, resistance heating evaporation, sputter method and so on, but the sputter method is preferably used. In this case,

though it is a unified sputter device, the catalyst of the present invention can be manufactured by putting components, added to Pd target, on each test piece and then sputtering them.

5 In addition, there is also a liquid coating method for making the catalyst, in which the catalyst of the present invention is made by coating blended solution of a first liquid containing Pd and a second liquid containing at least one element selected in
10 the group consisting of Fe, Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu on a substrate and then drying or heating it.

Now, an example of electron emitting device using carbon fiber formed using the catalytic
15 particles of the present invention is described with reference to schematic views shown in Figs. 1 and 2. At this time, the catalyst of the present invention is in a particle state for example.

Fig. 2A is a schematic plane view showing an
20 example of configuration of electron emitting device using the film containing a plurality of carbon fibers of the present invention, while Fig. 2B is a schematic sectional view taken along 2B-2B line of Fig. 2A.

25 In Figs. 2A and 2B, 201 denotes an insulation substrate, 202 denotes a drawer electrode (gate electrode), 203 denotes a cathode electrode, 207

denotes a carbon fibers, which is a material of an emitter, and 205 denotes a conductive material layer, which is made by growth of the carbon fiber 207 through the catalytic particles. This conductive
5 material layer 205 is not essential. Though the cathode electrode 203 is piled over the conductive material layer 205 on which the catalytic particles are arranged, it is also possible to arrange the catalyst of the present invention on a surface of the
10 cathode electrode 203 without the conductive material layer 205. In other words, it is also possible that the carbon fiber 207 is arranged on the surface of the cathode electrode 203.

As for the insulation substrate 201, an
15 insulation substrate using such as quartz glass of which surface is sufficiently cleaned can be used.

The gate electrode 202 and the cathode electrode 203 are conductive, and formed by a general vacuum film forming technique such as evaporation and
20 sputtering or a photolithography technique. As a material, carbon, metal, nitride of metal, carbide of metal and so on, which have heat resistance, are preferable.

The material of emitter (carbon fiber) 207 is
25 carbon fiber such as carbon nanotube, graphite nanofiber or the like, grown using the catalytic particles including Pd and additionally at least one

of Fe, Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu. Among the additional components, Fe, Co and Ni are preferably used to obtain effects of the present invention. And, particularly,

5 combination of Co and Pd is preferable. Also, it is required that Pd and the component (at least one of Fe, Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu) combined with Pd are alloyed in aspect of forming the carbon fiber of the present invention
10 having high uniformity and reproduction.

Hereinafter, an example of making the electron emitting element of the present invention shown in Fig. 2 is described in detail with reference to Fig. 1.

15 (Step 1)

After cleaning the substrate 101 sufficiently, an electrode layer with, for example, a thickness of 500nm is formed on the full substrate to form the gate electrode 102 and the cathode (emitter)
20 electrode 103. Quartz glass, glass partially replaced with K in which impurity contents of such as Na is reduced, a substrate in which SiO₂ is laminated on a silicon substrate, and a ceramic substrate of such as alumina can be used for the insulation
25 substrate 101.

Then, positive type photoresist is used to form resist pattern in a photolithography process. The

electrode layer is dry-etched using Ar gas while the patterned photoresist is used as a protective mask. Thus, the gate electrode 102 and the cathode electrode 103 with a gap (between the electrodes 102 and 103) 5 μ m are formed (Fig. 1A). Materials of the gate electrode 102 and the cathode electrode 103 are selected from, for example, carbon, metal, nitride of metal, carbide of metal, metallic boron, semiconductor and metal compound of semiconductor.

10 Materials of the gate electrode 102 and the cathode electrode 103 are preferably carbon, metal, nitride of metal, carbide of metal and so on, which have heat resistance. Thickness of the gate electrode 102 and the cathode electrode 103 may be set in range from

15 several tens of nm to several tens of μ m.

Hereinafter, patterning of film or resist using the photolithography process, film forming, lift-off, etching and so on is called simply as "patterning". (Step 2)

20 The resist pattern 104 is formed using negative type photoresist used for lift-off of an upper layer in the photolithography process (Fig. 1B).

Then, in this example, a conductive material layer 105 is formed on the cathode electrode. In

25 case of arranging the conductive material layer 105, it is preferred to use nitride of at least one of Ti, Zr, Ta and Nb as its material. Particularly, TiN is

preferred in aspect of growing the carbon fiber stably.

And then, the catalyst 106 of the present invention is formed on the conductive material layer 105 by using the above-described vacuum evaporation or liquid coating and so on (Fig. 1C). In order to arrange the catalyst of the present invention in a particle state, there can be used a method of spin coat of liquid containing ultrafine particles or a method of forming a catalytic layer by sputtering and then making it into particles by heating and aggregation under hydrogen circumstance. In the electron emitting device, the method using aggregation by heating under the hydrogen circumstance with assuring sufficient electric contact between the carbon fiber and the cathode electrode is preferred.

The catalytic particle of the present invention has a diameter 1nm or more and 100nm or lower, and more preferably 10 to 80nm. In order to make the catalyst having such a diameter, the catalyst is piled to a thickness of 1nm or more and 100nm or lower, and then heated under hydrogen circumstance. (Step 3)

By lifting off the conductive material layer 105 and the catalytic particle 106 on the resist through use of separation liquid of the resist

patterned in the process 2, the conductive material layer 105 and the catalytic particle 106 are patterned as desired (Fig. 1D).

(Step 4)

5 Then, the substrate on which the gate electrode 102, the cathode electrode 103 and the catalytic particle 106 are arranged is heat-treated under circumstance including gas having carbon. And, as for the gas having carbon, hydrocarbon gas is
10 preferably used. As for hydrocarbon gas, a gas selected among acetylene, ethylene, benzene and acetone is preferably used. And, it is also preferred that the hydrocarbon gas is in contact with the substrate 1 with being mixed with hydrogen. And,
15 such heating (heat treatment) is conducted at a temperature of 400°C or higher and 800°C or lower.

 If observing a surface of the conductive material layer 105 with SEM (a scanning electronic microscope) after such treatment, it would be
20 understood that a plurality of carbon fibers are formed (Fig. 1E). In the present invention, the region created by arrangement of a plurality of carbon fibers is called as "a film containing a plurality of carbon fibers". In the present
25 invention, fiber used for particularly the electron emitting element preferably has a diameter of 5nm or more and 100nm or lower, and more preferably 10 or

more and 30nm or lower. Deviating this range may cause decrease of the life and make it impossible to obtain sufficient emission current.

The electron emitting device using the film
5 containing a plurality of carbon fibers, as constructed above, is explained with reference to Figs. 3 and 4.

The device in which the gate electrode and the cathode electrode are spaced apart as much as a gap
10 of several μm is installed to a vacuum device 408 as shown in Fig. 3, and a vacuum exhaust device 409 exhausts gas until reaching at about 10^{-4}Pa . As shown in Fig. 3, the anode electrode 410 is installed to a height H of several mm from the substrate by using a
15 high voltage power source to apply high voltage V_a of several kVs (kilo-volts).

And, a phosphor 411 on which a conductive film is coated is installed to the anode 410.

At the device, device current I_f and electron
20 emission current I_e flowing by applying pulse voltage of about several ten V as driving voltage V_f are measured.

At this time, it is thought that an equipotential line 412 is formed as shown in Fig. 3.
25 A point where the electric field is most concentrated is considered to be an inner space of the gap from the anode 410 of an electron emitting material

(carbon fiber) designated by 413.

It is also thought that electrons are emitted from a plurality of carbon fibers positioned near the electric field concentrated point.

5 Electron emission characteristic of this electron emitting device is as shown in Fig. 4. In other words, I_e (electron emission density) is abruptly increased from threshold voltage (V_{th}), and not-shown I_f (current measured between the gate
10 electrode and the cathode) has similar characteristics to I_e , but its value is sufficiently low, compared with I_e .

In the embodiment of the present invention as described above, the gate electrode 102(202) and the
15 cathode 103(203) are arranged on a surface of the substrate 101(201).

The gap between the gate electrode 102(202) and the cathode 103(203) and the driving voltage (voltage applied between the gate electrode 2 and the cathode
20 3) are determined so that the electric field required for electron emission has a value 1 to 50 times of that of the horizontal electric field when comparing the vertical electric field required for electron emission from the carbon fiber with the vertical
25 electrical field required for electron emission.

At this time, "the horizontal electric field" in the present invention means "an electric field to

a direction substantially parallel to a surface of the substrate 101(201)" or "an electric field to a direction that the gate 102(202) and the cathode 103(203) are faced".

5 And, "the vertical electric field" mentioned above in the present invention means "an electric field to a direction substantially perpendicular to the surface of the substrate 101(201)" or "an electric field to a direction that the substrate
10 101(201) and the anode 411 are faced".

 As described above, Fig. 3 is a schematic sectional view showing configuration when the anode 411 is arranged upon the electron emitting device and then the electron emitting device is driven. As
15 shown in Fig. 3, in the electron emitting device of the present invention, assuming that a distance of the gap between the cathode 203 and the gate electrode 202 is d , a potential difference (voltage between the cathode 203 and the gate electrode 202)
20 when driving the electron emitting element is V_f , a distance between surfaces of the anode electrode 411 and the substrate 201 on which the elements are arranged is H , and a potential difference between the anode 411 and the cathode 203 is V_a , it is considered
25 that the electric field during driving (horizontal electric field; $E_1 = V_f/d$) is 1 times or more and 50 times or lower of the electric field between the

anode and the cathode (vertical electric field;
 $E_2 = V_a/H$). As a result, electrons emitted from the
cathode 203 collide with the gate electrode 202 may
be decreased. Therefore, it may obtain high
5 efficient electron emitting device with low spreading
of the emitted electron beam.

In addition, as shown in Figs. 2A, 2B and 3, in
the electron emitting device using the film
containing a plurality of carbon fibers of the
10 present embodiment, it is preferred that a plane,
which includes a surface of the film containing a
plurality of carbon fibers and is substantially
parallel to the surface of the substrate 201, is
arranged in a position spaced apart from the
15 substrate surface rather than the plane, which
includes a part of the surface of gate electrode 202
and is substantially parallel to the surface of the
substrate 202 in order to restrain scattering of
electrons on the gate electrode 202 or irradiation of
20 electrons toward the gate electrode.

In other words, in the electron emitting device
(electron emitting apparatus) of this embodiment, the
plane, which includes a part of the surface of the
film containing a plurality of carbon fibers and is
25 substantially parallel to the surface of substrate 1,
is arranged between the anode 411 and the plane,
which includes a part of the surface of the gate

electrode 202 and is substantially parallel to the substrate surface.

And, in the electron emitting device (electron emitting apparatus) of this embodiment, a front end
5 of the carbon fiber is arranged to a height "s" (which is defined as a distance between the plane, which includes a part of the surface of gate electrode 202 and is substantially parallel to the surface of substrate 201, and the plane, which
10 includes the surface of the film containing a plurality of carbon fibers and is substantially parallel to the surface of substrate 201), as shown in Fig. 3.

The mentioned height "s" depends on a ratio of
15 the vertical electrical field vs. the horizontal electrical field (the vertical electrical field/the horizontal electrical field), and the height is lowered as the ratio of the vertical electrical field vs. the horizontal electrical field is low, while
20 bigger height is required as the horizontal electric field is increased. Practically, the height "s" is in range of 10nm or more and 10 μ m or lower.

And, the electron emitting device using the film containing a plurality of carbon fibers of the
25 present invention may adopt various configurations in addition to the configuration shown in Figs. 2A and 2B.

For example, a cone-type emitter positioned in opening of the gate electrode of so-called Spindt-type electron emitting device as shown in Fig. 15 may be replaced with the film containing a plurality of carbon fibers. Or, it is also possible to arrange a film 4 containing a plurality of carbon fibers of the present invention on the cathode 3 arranged on the substrate 1 as shown in Fig. 14, position an anode 62 to be oriented to the substrate 1, and then apply electric field between the cathode 3 and the anode 62 so that electron may be emitted from the film 4 containing a plurality of carbon fibers of the present invention. Alternately, it is also possible in the configuration of the electron emitting element that a grid electrode for controlling electron emission is additionally positioned between the anode and the film containing a plurality of carbon fibers arranged on the cathode.

However, in the present invention, it is preferred to have configuration that the gate electrode and the cathode are arranged spaced apart on the substrate 1 so that the film containing a plurality of carbon fibers is positioned on the cathode, as shown in the sectional view of Fig. 2. By using the configuration of Figs. 2A and 2B, it is possible to obtain the electron emitting device with high efficiency and lower spreading of the emitted

electron beam.

In addition, though it is shown in Fig. 2 that the gate electrode 202 and the cathode 203 have identical thickness, the cathode may have greater
5 thickness than that of the gate electrode in other configurations. Additionally, such configuration can be modified even if an insulation layer with a suitable thickness is arranged between the cathode and the substrate.

10 As for preferable content of Co included in the catalyst, the inventors have conducted investigation for different content of Co. As a result, it has been found that voltage width (amplitude voltage width) and threshold required for obtaining certain
15 current is varied depending on concentration of Co. As a result, in the viewpoint of increased threshold and voltage width required to obtain certain current from carbon fiber, it is preferred to add at least 20% of Co to Pd. And, if a fraction of Co is less
20 than 20atm%, it is impossible to obtain good electron emission characteristic for a long time in the formed electron emitting device using the film containing a plurality of carbon fibers. In addition, it has been found that a minimum growth temperature of carbon
25 fiber can substantially not obtained with a general substrate if a fraction of Co in the catalyst containing Pd and Co exceeds 80atm%. It has also

been found that, if a fraction of Co exceeds 80atm%, stability is better but the electron emission characteristic is deteriorated. As a result, a fraction of Co in the catalyst containing Pd and Co is 20atm% or more and 80atm% or lower.

As a specific example, a measurement system is configured composed of parallel plate and so on by electrically connecting and the carbon fibers grown with different content (0%, 23%, and 50%) of Co added to Pd and then positioning them in a vacuum chamber, and then applying high positive voltage to a faced anode. Fig. 9 shows results measuring electron emission amounts emitted from the fiber in one embodiment of the present invention.

As shown in Fig. 9, in this example, one having the smallest amplitude voltage width (width of voltage required for obtaining certain current as the electron emission current I_e increases from zero) is Co: 50atm% for the smaller one. As this amplitude voltage width is smaller, cost for the device required for driving control is decreased. In detail, as a result of investigation with changed added contents, the amplitude voltage width is effectively lowered rather than the case of 100% of Pd when Co is or more 20atm%. Therefore, the cost of driving device is reduced as the threshold is lower even for an increased threshold. As apparently understood in

Fig. 9, it is observed that the threshold is lowered as the content of Co to Pd is increased.

On the other hand, a maximum content of Co to Pd is investigated in another aspect. In order to dissolve hydrocarbon gas using the catalyst, an oxidized film existing on a surface of the catalyst should be removed. Though the oxidized film is removed by exposing the catalyst to high temperature by using such as hydrogen, this removing temperature becomes one of factors determining the lowest limit of growth. After investigating the lowest limit of growth, the inventors have found that the lowest limit is about 400°C at Pd: 100%, but about 410°C at Co: 23atm%, about 500°C at Co: 50atm% and about 600°C at Co: 100%. As a result of investigation with more modified content of Co in more detail, it has been found that the minimum growth temperature is abruptly increased when a fraction of Co exceeds 80atm%, which is substantially equal to the case of Co: 100%.

As easily understood from the results, when using the carbon fiber grown from the catalytic particles using materials including Pd and Co (more specifically, alloy of Pd and Co), a preferable concentration of Co is 20 to 80atm%. Such a preferable range of concentration is equal for Fe and Ni, which are materials to be added to Pd.

Now, the image forming apparatus obtained by

arranging a plurality of electron emitting elements to which the present invention is applicable is described with reference to Figs. 5 and 6. In Fig. 5, 601 denotes an electron source substrate, 602 denotes
5 X-directional wire, 603 denotes Y-directional wire, 604 denotes the electron emitting device of the present invention and 605 denotes a wire connection.

In Fig. 5, m number of X-directional wires are composed of DX_1, DX_2, \dots, DX_m . Material, film
10 thickness and width are suitably designed. The Y-directional wires 603 includes n number of wires DY_1, DY_2, \dots, DY_n , identical to the X-directional wire 602. An insulation interlayer, not shown, is arranged between m number of the X-directional wires 602 and n
15 number of the Y-directional wires 603 to separate them electrically (m and n are all positive integer).

The X-directional wire 602 and the Y-directional wire 603 are all drawn out as external terminals, respectively.

20 A pair of electrodes (not shown) composing the electron emitting device 604 of the present invention is electrically connected through the wire connections 605 to m number of the X-directional wires 602 and n number of the Y-directional wires 603.

25 A scanning signal applying means, not shown, for applying scanning signals is connected to the X-directional wire 602 in order to select a row of the

electron emitting device 604 of the present invention arranged to X direction. On the other hand, a modulated signal generating means, not shown, for modulating each column of the electron emitting
5 device 604 of the present invention, depending on an input signal, arranged to Y direction is electrically connected so as to select individual device to be independently operated.

Such an image forming apparatus composed using
10 the electron source in a simple matrix arrangement is described with reference to Fig. 6. Fig. 6 shows a display panel of the image forming apparatus.

In Fig. 6, 701 denotes an electron source substrate in which a plurality of electron emitting
15 devices are arranged, 703 denotes a rear plate to which the electron source substrate 701 is fixed, and 710 denotes a face plate in which a fluorescent film 708 and a metal back 707 are formed on inside of a glass substrate 709. 704 is a support frame, which
20 is connected to the rear plate 703 and the face plate 710. 711 denotes an envelope, which is sealed.

706 denotes the electron emitting device of the present invention. 702 and 705 denote X-directional wire and Y-directional wire connected to the electron
25 emitting device of the present invention.

The envelope 711 includes the face plate 710, the support frame 704 and the rear plate 703, as

described above. On the other hand, the envelope 711 has strength sufficient against atmosphere pressure by installing supports (not shown) called as spacer to the face plate 710 and the rear plate 703.

5 The configuration of the image forming apparatus described above is just an example of image forming apparatus applicable to the present invention, and can be modulated depending on technical aspects of the present invention. As for an input signal, TV
10 signal (for example, high qualified TV including MUSE manner) as well as NTSC manner, PAL, SECAM manner and so on can be adopted.

 In addition, the carbon fiber obtained in the present invention can be preferably applied to body
15 for storing a material (ex. hydrogen), cathode material of batteries and complex materials as well as the electron emitting device. Particularly, in case the carbon fiber of the present invention is graphite nanofiber, since graphene having excellent
20 crystallization to an axial direction of fiber is accumulated, more superior hydrogen occlusion (in other words "adsorption" or "storage") is come out, and better characteristics can be obtained as a cathode material of batteries. Among batteries, the
25 graphite nanofiber of the present invention is preferably applied to cathode of a secondary battery (rechargeable battery), and in particular the

graphite nanofiber of the present invention having excellent crystal structure is preferably applied to cathode of a lithium ion secondary battery. Since the graphite nanofiber of the present invention has
5 excellent crystal structure, this may form stable and large charging/discharging capacity. And when the graphite nanofibers formed using the catalytic particle mainly containing at least one of a Fe-Pd alloy, a Ni-Pd alloy and the Co-Pd alloy are applied
10 to a body for storing hydrogen or secondary battery, the especially excellent characteristic can be shown.
(Examples)

Hereinafter, examples of the present invention are described in detail.

15 <Example 1>

In the first Example, Pd and Co are added as catalyzing particles by the common sputtering manner.

Now, a method of making electron emitting device of the present example is described in detail
20 with reference to Figs. 1A to 1E.

(Step 1)

After cleaning the substrate 101 sufficiently with the quartz substrate, Ti with thickness of 5nm and Pt with thickness of 100nm, not shown, are
25 continuously evaporated on overall substrate by sputtering at an initial stage in order to form the gate electrode 102 and the cathode (emitter)

electrode 103.

Then, the resist pattern is formed using a not-shown positive type photoresist in the photolithography process.

5 Then, the patterned photoresist as mask is dry-etched by using Ar gas on the Pt layer and Ti layer, and the gate electrode 102 and the cathode 103 having an electrode gap (width of interval) of $5\mu\text{m}$ is patterned (Fig. 1A).

10 (Step 2)

The resist pattern 104 is formed using negative type photoresist used for afterward lift-off of an upper layer in the photolithography process (Fig. 1B).

15 Then, TiN layer is formed as a conductive material layer on which carbon fiber 107 will be grown with the catalytic particles 106.

In addition, the catalytic particles 106 of the present invention are all formed by common sputtering manner. In this case, some Co thin peaces are putted
20 on a Pd sputtering target. The catalytic particles 106 include Pd and Co of 33atm% in a ratio (atomic ratio) to Pd (Fig. 1C).

(Step 3)

The resist and the conductive material layer
25 105 and the catalytic particle 106 on the resist are lifted off by using separation liquid of the resist patterned in the process 2, and the conductive

material layer 105 and the catalytic particle 106 are patterned as desired (Fig. 1D).

(Step 4)

Then, they are heated in ethylene gas flow.

5 After investigation with a scanning electronic microscope, it is found that a plurality of carbon fibers are formed. (Fig. 1E) Moreover, the carbon fibers were graphite nanofibers.

The electron emitting device made as above are
10 mounted in a vacuum device as shown in Fig. 3, and gas is exhausted by the vacuum exhausting device 409 until reaching to 2×10^{-5} Pa. Positive voltage $V_a = 10$ kV is applied to the anode 411 H=2mm spaced apart from the device as shown in Fig. 3. At this time, device
15 current I_f and electron emission current I_e flowing by applying pulse voltage having driving voltage V_f are measured at the device.

I_f and I_e characteristics of the device are shown in Fig. 4. In other words, I_e is abruptly
20 increased at about half of the applied voltage, and about $1 \mu\text{A}$ of the electron emission current I_e is measured when V_f is 15V. On the other hand, though I_f has similar characteristics to I_e , but its value is low more than one order, compared with I_e .

25 <Example 2>

In the second embodiment, Pd and Fe are added as catalytic particles by common co-evaporation

method.

In the present embodiment, after making the electron emitting device in a similar manner to the first embodiment, except that the second process is
5 conducted as below, I_f and I_e are measured.

(Step 2)

The resist pattern 104 is formed using negative type photoresist used for lift-off of an upper layer in the photolithography process (Fig. 1B).

10 Then, TiN layer is formed as a conductive material layer 105 on which the carbon fiber 107 would be grown with the medium of the catalytic particles 106.

And, the catalytic particles 106 of the present
15 invention are formed by a common electron beam (two materials simultaneously) evaporation manner as follows. Then, the catalytic particles are deposited on TiN layer by using Pd and Fe as vacuum evaporation sources. As a result, the catalytic particles 106
20 containing Fe component of 20atm% to Pd is formed in an island shape (Fig. 1C).

I_f and I_e characteristics of the device are identical to those of Fig. 4. In other words, I_e is abruptly increased at about half of the applied
25 viltage, and about $1\mu A$ of the electron emission current I_e is measured when V_f is 15V. On the other hand, though I_f has similar characteristics to I_e , but

its value is low more than one order, compared with I_e . Moreover, the carbon fiber formed in this example was a graphite nano fiber.

<Example 3>

5 In the third embodiment, Pd and Ni are added as catalytic particles by liquid coating.

 In the present embodiment, after making the electron emitting element in a similar manner to the first embodiment, except that the second process is
10 conducted as below, I_f and I_e are measured.

(Step 2)

 The resist pattern 104 is formed using negative type photoresist used for lift-off of an upper layer in the photolithography process (Fig. 1B).

15 Then, TiN layer is formed as a conductive material layer 105 on which the carbon fiber 107 would be grown with the medium of the catalytic particles 106.

 And, the catalytic particles 106 of the present
20 invention are formed by liquid coating as follows. By using mixed solution of acetic acid complex of Pd and Ni, the mixed liquid is spinner-coated. After coating, it is heated at the atmosphere. As a result, the catalytic particles 106 containing Ni component
25 of 25atm% to Pd is formed in an island shape (Fig. 1C).

I_f and I_e characteristics of the element are

identical to those of Fig. 4. In other words, I_e is abruptly increased at about half of the applied voltage, and about $1\mu\text{m}$ of the electron emission current I_e is measured when V_f is 15V. On the other
5 hand, though I_f has similar characteristics to I_e , but its value is low more than one order, compared with I_e . Moreover, the carbon fiber formed in this example was a graphite nano fiber.

<Example 4>

10 In this embodiment, the electron emitting device shown in Figs. 1 and 2 is used, like the first embodiment. And, in this embodiment, the cathode 203(103) is coated with TiN (titan nitride) with thickness of 300nm by using the ion beam sputtering
15 manner. The conductive material layer 105 used in the first embodiment is not used.

And, a catalytic layer made of Pd-Co alloy is evaporated on the cathode as much as amount to be an island shape by the sputtering manner using Ar
20 (argon) gas. As a result of analysis of the evaporated catalytic layer, it is found that 50atm% of Co is included in Pd. After that, the catalytic particles 106 with particle diameter of about 50nm are obtained though heating under hydrogen
25 circumstance.

Then, in this embodiment, the substrate is heated at 500°C for 10 minutes among gas flow after

mixing 1% of hydrogen diluted by nitrogen and 0.1% of acetylene diluted by nitrogen in 1:1 ratio at atmosphere pressure (about 1×10^5 Pa).

As a result of observing that with the scanning
5 electronic microscope, it is found that a plurality of carbon fibers, curved and elongated in a fiber shape with diameter of about 50nm, are formed in a region where Pd-Co particles are formed. At this time, the layer composed of a plurality of carbon
10 fibers has thickness of about 5 μ m. In addition, as a result of observing this material with the transmission electronic microscope, the image as shown in Fig. 8 is obtained. In Fig. 8, a shape of carbon fiber seen at an optical microscope level
15 (~1000 times) are schematically shown to left, a shape at an scanning electron microscope (SEM) level (~30,000 times) to center, and a shape at a transmission electron microscope (TEM) level (~1,000,000 times) to right.

20 And, an interlayer spacing d(002) is inferred to be 0.35 to 0.37nm. In addition, in the center of fiber axis, there exist an element in which the graphene layer is omitted and an element which is not distinct (it is certainly filled with carbon in
25 amorphous shape).

As a result of measuring electron emission characteristic (voltage-current characteristic) of

this device, the characteristics shown in Fig. 4 are obtained and the threshold electric field required for electron emission is $3\text{V}/\mu\text{m}$.

<Example 5>

5 In this embodiment, the electron emitting device shown in Figs. 1 and 2 is used, like the first embodiment. And, in this embodiment, the cathode 203(103) is coated with Cr (chrome) with thickness of 300nm by using the ion beam sputtering manner.

10 And, in this embodiment, titan (Ti) is sputter-evaporated as a conductive material layer 105(205) to have thickness of 5nm. And, Pd (Co 25atm%) to be the catalytic layer is sputter-evaporated to have an island shape with thickness less than 5nm. After
15 that, the catalytic particles 106 are formed by heat treatment under hydrogen circumstance.

 And, in this embodiment, after putting the substrate into a furnace and then exhausting gas in the furnace sufficiently, gas in which 1vol% of
20 hydrogen is diluted by nitrogen and 1% of ethylene diluted by nitrogen are put into the furnace in approximately 1:1 ratio up to pressure of 400Pa.

 Then, in this embodiment, as a result of heating the furnace up to 600°C and then maintaining
25 the temperature for 30 minutes, carbon fibers having a film shape are grown on the cathode. As a result of observing this carbon fibers with the transmission

electronic microscope, the configuration shown in Fig. 16 is checked.

As a result of measuring electron emission characteristic (voltage-current characteristic) of this device, the characteristics shown in Fig. 4 are obtained and the threshold electric field required for electron emission is $5\text{V}/\mu\text{m}$.

<Example 6>

After sufficiently cleaning the quartz substrate 1, TiN is coated to have thickness of 300nm as the cathode by using the ion beam sputtering manner.

Then, the layer in which catalytic particles composed of Pd-Co alloy are dispersed and arranged by the sputtering manner using Ar gas are evaporated on the cathode with size of 1mm^2 . After that, heat treatment under hydrogen circumstance forms a plurality of catalytic particles composed of Pd-Co alloy with particle diameter of about 30nm.

The formed catalytic particles are composed of alloy in which 50atm% of Co is contained in Pd, as a result of analysis.

Then, the substrate is heat-treated at 600°C for 10 minutes at about atmosphere pressure (about $1 \times 10^5\text{Pa}$) through flow of gas (gas in which 1vol% of hydrogen is mixed with nitrogen and gas in which 1vol% of ethylene is mixed with nitrogen are mixed in

1:1 ratio).

As a result of observing a surface of the cathode with the scanning electronic microscope, it is found that a plurality of graphite nanofibers
5 107(207), curved with diameter of 30~50nm and grown in a fiber shape, are formed on the cathode. At this time, the layer composed of a plurality of graphite nanofibers has thickness of about 5 μ m.

And, an interlayer spacing d(002) is measured
10 to be 0.35nm.

In addition, in the center of the fiber, there exist an element in which the graphene layer is omitted and an element which is not distinct.

As a result of measuring Raman spectrum
15 characteristic by irradiating laser rays with wavelength of 514.5nm on the graphite nanofibers, the result is as shown in Fig. 10.

From this result, it is found that FWHM 1 is 68kaiser(cm^{-1}), FWHM 2 is 55kaiser(cm^{-1}) and h_2/h_1 is
20 2.2.

On the other hand, when being replaced with the catalyst containing 100% of Pd without adding Co and the catalyst containing 23atm% of Co added to Pd, the film containing a plurality of carbon fibers is
25 formed using each catalytic particle, identically to this embodiment.

And, the electron emission characteristics of

the film formed using the catalyst containing 50atm% of Co added to Pd prepared in this embodiment, the film formed using the catalyst containing 100% of Pd and the film formed using the catalyst containing
5 23atm% of Co added to Pd are compared. Their comparison results are schematically shown in Fig. 12.

Fig. 12A shows results of Raman spectrum measurement obtained by irradiating laser with wavelength of 514.5nm on the carbon fiber formed
10 using the catalyst containing 100% of Pd without adding Co.

Likewise, Fig. 12B shows results of Raman spectrum measurement obtained by irradiating laser with wavelength of 514.5nm on the carbon fiber formed
15 using the catalyst containing 23atm% of Co added to Pd.

And, Fig. 12C shows results of Raman spectrum measurement obtained by irradiating laser with wavelength of 514.5nm on the graphite nanofiber
20 formed using the catalyst containing 50atm% of Co added to Pd, prepared in this embodiment.

As shown in Fig. 14, a substrate 1 on which a film 4 containing a plurality of carbon fibers arranged on the cathode 3 prepared in this embodiment
25 is positioned in a vacuum chamber 9. In Fig. 14, 1 denotes the substrate, 3 denotes the cathode, 4 denotes the film containing a plurality of carbon

fibers, 61 denotes an anode substrate, 62 denotes a transparent anode using ITO, 5 denotes an insulating spacer, 6 denotes an ammeter, 7 denotes a high voltage power source, 8 denotes a vacuum pump and 9 denotes the vacuum chamber. A glass substrate 61 to which a transparent electrode is attached through the insulating spacer 5 is installed. The high voltage power source 7 and the ammeter 6 are respectively connected thereto, and inner pressure of the vacuum chamber 9 is set to 1×10^{-9} Pa of vacuum level by using the vacuum pump 8.

And, high voltage V_a is applied to the anode 62, and then electron emission amount emitted from the each film containing carbon fibers formed with different content of Co to Pd is measured by the ammeter 6. And at the same time, time dependence (life characteristic) of electron emission characteristics of the each film containing carbon fibers is measured.

At this time, it is assumed that three kinds of films corresponding to Figs. 12A to 12C have same thickness.

In addition, in the present invention, current density when electron emission current does not increase in exponential relation though voltage increases in view of V-I characteristic when voltage of the anode is increased slowly is defined as a

maximum current density of the each film.

And, in the first place, the maximum current density is measured for the each film, and set to as an initial value of the maximum current density. And, 5 change of current density to time when voltage achieving the initial value of the maximum current density is continuously applied to the each film is measured.

Results of investigation for change of life by 10 measuring current density change of each film are indicated by (1) to (3) in Fig. 12, each of which corresponds to (a) to (c) of Fig. 12 respectively.

In the graphite nanofiber film ((3) in Fig. 12) of this embodiment, the current at a maximum current 15 density is $80\text{mA}/\text{cm}^2$ and falloff of the current is maintained at an approximately constant value. However, in the carbon fiber film ((2) in Fig. 12) in which only 23atm% of Co is added to Pd, though an initial value of current density is equal to that of 20 the graphite nanofiber film((3) in Fig. 12) of this embodiment, the electron emission characteristic is rapidly decreased. In addition, in the carbon fiber film ((1) in Fig. 12) in which no Co is added to Pd, an initial value of current density is less than the 25 case of this embodiment and the electron emission characteristic is also rapidly decreased.

And, in the measurement system shown in Fig. 14,

density of the electron emission site is $10^3/\text{cm}^2$ or more when an electric field of $1 \times 10^5 \text{V/cm}$ is applied to the film (Co: 50atm%) prepared in the present embodiment. In addition, $10^3/\text{cm}^2$ or more of graphite
5 nanofibers are arranged in the film (Co: 50atm%) prepared in this embodiment.

In addition, since a definite peak is not observed in the film containing carbon fibers shown in (a) of Fig. 12, it is difficult to define height
10 of peak (Raman scattering intensity) and FWHM.

In the film containing carbon fibers shown in (b) of Fig. 12, definite peaks are observed near $1355 \text{kaiser} (\text{cm}^{-1})$ and near 1580kaiser . However, the FWHM is wider in the portion shown near 1355kaiser
15 than that shown near 1580kaiser .

In the film containing graphite nanofibers prepared in this embodiment shown in (c) of Fig. 12, Raman spectra has a first peak in a range of $1355 \pm 10 \text{kaiser}$ and a second peak in a range of $1580 \pm 10 \text{kaiser}$. And, the FWHM of the peak shown in $1355 \pm 10 \text{kaiser}$ is narrower than that shown in $1580 \pm 10 \text{kaiser}$. In addition, the height of peak shown in $1355 \pm 10 \text{kaiser}$ (relative intensity which is difference between background intensity and Raman
25 scattering intensity of peak shown in $1355 \pm 10 \text{kaiser}$) is about double of the height shown in $1580 \pm 10 \text{kaiser}$ (relative intensity which is difference

between background intensity and Raman scattering intensity of peak shown in 1580 ± 10 kaiser).

And, in the film containing graphite nanofibers prepared in this embodiment shown in (c) of Fig. 12, it is found in Raman spectra that relative intensity h_3 , which is difference between background intensity and minimum intensity of Raman scattering intensity between the first peak and the second peak (or between D band and G band), is $1/10$ or lower of relative intensity h_2 , which is difference between background intensity and Raman scattering intensity of the first peak.

From these results, it is found that deterioration of the electron emission characteristics closely related to the FWHM of each peak and the peak height in Raman spectra.

Therefore, after measuring life characteristic of the films containing a plurality of carbon fibers in various types by changing element added to Pd, growth hours and concentration of gas, preferably applied in the present invention, there is caused improvement of initial electron emitting current density in Raman spectrum characteristic in the fact that the relative intensity h_2 , which is difference between background intensity and Raman scattering intensity of the first peak, is 1.3 times or more of the relative intensity h_1 , which is a

difference between Raman scattering intensity of the second peak and background intensity.

And, in the fact that the relative intensity h_2 , which is difference between background intensity and Raman scattering intensity of the first peak, is 1.3 times or more and 2.5 times or lower of the relative intensity h_1 , which is a difference between Raman scattering intensity of the second peak and background intensity, improvement of initial current density and life is obtained.

In addition, the film containing a plurality of carbon fiber of the present invention may obtain improvement of initial current density and life when the Full-Width Half-Maximum of the first peak (FWHM2) and the Full-Width Half-Maximum of the second peak (FWHM1) satisfy the condition that $FWHM2/FWHM1 \leq 1.2$.

And preferably in the film containing a plurality of carbon fibers of the present invention, the Full-Width Half-Maximum of the first peak (FWHM2) and the Full-Width Half-Maximum of the second peak (FWHM1) are in relation that $FWHM2/FWHM1 \leq 1.2$, and the relative intensity h_2 , which is difference between background intensity and Raman scattering intensity of the first peak, is 1.3 times or more of the relative intensity h_1 , which is a difference between Raman scattering intensity of the second peak and background intensity. And more preferably,

the film containing a plurality of carbon fibers of the present invention may obtain improvement of initial current density and life when the Full-Width Half-Maximum of the first peak (FWHM2) and the Full-Width Half-Maximum of the second peak (FWHM1) are in relation that $FWHM2/FWHM1 \leq 1.2$, and the relative intensity h_2 , which is difference between background intensity and Raman scattering intensity of the first peak, is 1.3 times or more and 2.5 times or lower of the relative intensity h_1 , which is a difference between Raman scattering intensity of the second peak and background intensity.

And further preferably, the film containing a plurality of carbon fibers of the present invention may obtain stable electron emission current density when relative intensity h_3 , which is difference between background intensity and minimum intensity of Raman scattering intensity between the first peak and the second peak (or between D band and G band), is 1/10 or lower of relative intensity h_2 , which is difference between background intensity and Raman scattering intensity of the first peak in addition to each of above characteristics (relation of FWHM of the first peak and the second peak and/or relation of intensity ratio of the first peak and the second peak). And, it is possible to obtain high electron emission current density stably for a long time when

the relative intensity h_3 is $1/15$ or lower of the relative intensity h_2 .

And, the film containing a plurality of carbon fiber may obtain stable and high electron emission current density for a long time by restrain decrease of high initial electron emission current density when FWHM1 and FWHM2 have a relation that $FWHM2/FWHM1 \leq 1.2$, h_2 is 1.3 times or more and 2.5 times or lower of h_1 , and h_3 is $1/15$ or more of h_2 .

After evaluating the graphite nanofiber of the present invention shown in (c) of Fig. 12 and the carbon fiber shown in (a) and (b) of Fig. 12 in view of hydrogen storing and cathode material of lithium ion battery, the graphite nanofiber shown in Fig. 12C of the present invention has more excellent hydrogen storing than the carbon fiber shown in Figs. 12A and 12B. the carbon fiber shown in Fig. 12B of more excellent hydrogen storing than the carbon fiber shown in Figs. 12A.

And, when absorption and desorption of hydrogen are repeated, the graphite nanofiber shown in (C) of Fig. 12 of the present invention shows more stable absorption and desorption characteristics than the carbon fiber shown in (a) and (b) of Fig. 12. And the absorption and desorption characteristics of the carbon fibers shown in (b) of Fig. 12 is more stable than the carbon fibers shown in (b) of Fig.

12.

In addition, a carbon electrode (cathode) is made using a plurality of graphite nanofibers shown in (c) of Fig. 12 of the present invention, and a
5 carbon electrode (cathode) is made using a plurality of carbon fiber shown in (a) and (b) of Fig. 12. And, charging capacity and discharging capacity of each cathode are measured with a common test battery. As a result, the carbon electrode (cathode) using a
10 plurality of graphite nanofiber shown in (c) of Fig. 12 of the present invention shows particularly superior characteristics. And the carbon electrode (cathode) using a plurality of carbon fiber shown in Fig. 12B shows superior charging/discharging capacity
15 than that of using a plurality of carbon fiber shown in Fig. 12C.

And, after repeating such charging and discharging, the carbon electrode (cathode) using a plurality of graphite nanofiber shown in (c) of Fig.
20 12 of the present invention shows significantly stable charging/discharging characteristic and rapid charging characteristic at the same time. And the carbon electrode (cathode) using a plurality of carbon fiber shown in Fig. 12B shows superior
25 stability of charging/discharging capacity than that of using a plurality of carbon fiber shown in Fig. 12C.

The cathode made in this embodiment is used as a cathode of a lithium ion secondary battery for measurement. At this time, lithium transitional metal oxide is used as anode active material for the
5 anode.

In order to make the cathode with graphite nanofibers of the present invention, a plurality of the graphite nanofibers of the present invention may be made into a pellet shape by using such as binder.

10 The cathode using the graphite nanofiber of the present invention may be preferably applied to the lithium ion secondary battery as a secondary battery(rechargeable battery). In addition, as a cathode material, a transitional metal is preferably
15 included. And, as electrolytic solution, any one which is commonly used for the lithium ion secondary battery will do.

<Example 7>

This Example is different from the above
20 embodiment in fact of Pd (70atm% of Ni is added) is used for the catalyst instead of the catalyst of the Example 6 and in fact of carbon fiber forming method.

In order to form carbon fiber, a substrate having the catalytic particles arranged on the
25 cathode made of TiN is put into a furnace, and then after exhausting gas in the furnace sufficiently, gas in which 1vol% of hydrogen is mixed with helium (He)

and gas in which 1vol% of ethylene is mixed with helium are put in the furnace at near 1:1 ratio to have inner pressure of 400Pa.

Then, the above furnace is heated to 600°C and
5 maintained at the temperature for 30 minutes so that same graphite nanofiber as in the 6th embodiment is grown.

After measuring Raman spectrum characteristic by irradiating laser of 514.5nm to this graphite
10 nanofibers as well as in the Example 6, the results as shown in Fig. 11 are obtained.

From those results, FWHM1 is 70kaiser(cm^{-1}), FWHM2 is 55kaiser and h_2/h_1 is 1.8, all of which satisfy relation of FWHM and intensity ratio of
15 Raman scattering.

Then, identically to the Example 6, time dependency (life characteristic) of electron emission amount emitted from the film containing the graphite nanofibers of this embodiment is measured.

20 As a result, though emission current at the maximum current density is higher than that of the device(film) of the Example 6 ((3) of Fig. 12), decrease of emission current density takes more time for going to a constant value, compared with the
25 device of the Example 6 ((3) of Fig. 12). However, it obtains characteristics superior to the devices of (2) of Fig. 12 or (1) of Fig. 12 in the Example 6,

and close to the device of the Example 6.

And, in the film containing a plurality of graphite nanofibers prepared in this Example also, density of the electron emission site is more than
5 $10^3/\text{cm}^2$ when an electric field of $1 \times 10^5 \text{V/cm}$ is applied, according to the measurement system shown in Fig. 14 by using same measuring method as the Example 6. In addition, $10^3/\text{cm}^2$ of graphite nanofibers are arranged in the film prepared in this Example.

10 <Example 8>

This Example is different from the Example 6 in fact that Ni-Pd is used as an element composing catalyst and in fact of carbon fiber forming method.

First of all, Pd-Ni catalyst is made by putting
15 several scales (about 2cm square) containing 100% of Pd upon a sputtering target made of 100% of Ni of a sputter-evaporating device and then sputtering them at the same time, and about 4nm of film made of Pd-Ni is evaporated on TiN cathode. And, by adjusting
20 ratio of Pd scales put on Ni, there are prepared films respectively containing 20atm% of Ni, 50atm% of Ni and 80atm% of Ni to Pd.

In addition, there is separately prepared a substrate in which Pd film with a thickness of 4nm is
25 evaporated on TiN cathode by preparing only a sputtering target having 100% of Pd.

Then, Pd 100%, Pd-Ni(20atm%), Pd-Ni(50atm%),

Pd-Ni(80atm%) and Ni 100% substrates formed as above are put into an infrared furnace (IR furnace), and hydrogen (2%) diluted by inert gas and ethylene (C_2H_4 , 2%) diluted by inert gas are flowed in at 1:1 ratio, then the furnace maintained at 580°C for about 5 minutes and then cooled.

5 kinds of substrates are respectively cut and photographed by SEM, and a thickness of the film containing a plurality of carbon fibers is measured. In addition, for the film containing a plurality of carbon fibers formed on each substrate, Raman spectrum characteristic(Raman spectrum) detected by irradiating laser with a wavelength of 514.5nm is measured as well as the embodiment 6. Each value of FWHM1, FWHM2, h1, h2, h3 and film thickness at this time is subscribed in the following Table 1.

(Table 1)

| atm% \ | h1 relative value | h2 relative value | h3 relative value | FWHM1 kaiser | FWHM2 kaiser | film thickness μm |
|--------------|-------------------------|-------------------------|-------------------------|-----------------|-----------------|------------------------------|
| Pd 100% | 52 | 46 | 39 | >150 | >200 | ~3 |
| Pd-Ni 20% | 52 | 44 | 22 | 94 | 208 | ~3 |
| Pd-Ni 50% | 52 | 66 | 12 | 60 | 75 | ~1 |
| Pd-Ni 80% | 52 | 60 | 17 | 65 | 78 | ~1 |
| Ni 100% | 52 | 45 | 17 | 70 | 80 | very thin |

As seen in Table 1, though carbon fiber grows in this conditions when Pd is 100%, it is surmised from the FWHM of Raman peak (measured from a curve fitting to Lorenz curve) caused by graphite configuration that the carbon fiber formed with Pd100% having less structural order than that of the other carbon fibers.

Carbon fiber is checked to grow when Ni is added to Pd in range of 20atm% to 100atm%. However, very small number of carbon fiber is grown when Ni is 100%, and its length is also less than several hundred nm. In addition, it is recognized that the FWHM (FWHM1 and FWHM2) are significantly decreased by adding Ni.

And then, time dependence (life characteristic) of electron emission amount emitted from the film containing the graphite nanofibers of this Example in the same condition as the Example 6 is measured.

As a result, all of devices(films) comprising a plurality of carbon fibers formed using the catalytic particles of Pd-Ni alloy show electron emission characteristic near (2) of Fig. 12 shown in the Example 6. And, the catalytic particles having 100% of Ni shows low growth of carbon fiber, and very low electron emission current, compared with other devices. On the other hand, the device comprising a plurality of carbon fibers formed using the catalytic

particles having 100% of Pd shows electron emission characteristic substantially equal to (1) of Fig. 12 shown in the sixth embodiment. From those results, it is determined that an effective range of Ni addition is 20atm% to 80atm%.

<Example 9>

A result that Co is added to Pd in same manner as the eighth embodiment is shown in Table 2. Method of making catalyst and growth condition of carbon fiber are identical to the Example 8.

(Table 2)

| Atm% Pd-Co | h1 relative value | h2 relative value | h3 relative value | FWHM1 kaiser | FWHM2 kaiser | film thickness μm |
|---------------|-------------------------|-------------------------|-------------------------|-----------------|-----------------|-------------------------|
| 20% | 52 | 38 | 12 | 119 | 196 | ~3 |
| 50% | 52 | 47 | 7 | 50 | 112 | ~1 |
| 80% | 52 | 49 | 7 | 45 | 90 | ~1 |

And, in a test piece having 100% of Co, growth is not checked at the 580°C (growth temperature) . In addition, it is found that the FWHM s (FWHM1 and FWHM2) are significantly decreased when Co is added 20atm% or more.

Then, time dependence (life characteristic) of electron emission amount emitted from the carbon fiber of this Example in the same condition as the Example 6 is measured.

As a result, all of devices comprising a plurality of carbon fibers formed using the catalytic particles of Pd-Co alloy show electron emission characteristic near (2) of Fig. 12 shown in the Example 6, but worse than the electron emitting device prepared in the Example 6 (the characteristic is shown in (3) of Fig. 12. And, the catalytic particles having 100% of Co shows low growth of carbon fiber and low electron emission characteristic.

On the other hand, the device using a plurality of carbon fibers formed using the catalytic particles having 100% of Pd shows electron emission characteristic equal to (1) of Fig. 12 shown in the Example 6. From those results, it is determined that an effective range of Co addition is 20atm% to 80atm%.

<Example 10>

In this Example, growth temperature of carbon fiber in the Example 8 is changed from 580°C to 630°C. Others are identical to the Example 8. Its results are shown in Table 3.

(Table 3)

| atm% \ | h1 relative value | h2 relative value | h3 relative value | FWHM1 kaiser | FWHM2 kaiser |
|--------------|-------------------------|-------------------------|-------------------------|-----------------|-----------------|
| Pd-Ni 20% | 52 | 79 | 12 | 63 | 73 |
| Pd-Ni 50% | 52 | 112 | 7 | 59 | 52 |
| Pd-Ni 80% | 52 | 89 | 7 | 56 | 59 |
| Ni 100% | 52 | 50 | 7 | 50 | 55 |

And, growth in a test piece having 100% of Ni is better than that of the Example 9, but the growth of carbon fiber is very slow, compared with the case that particles of Pd-Ni alloy are used. In addition,
5 it is found that the FWHM s (FWHM1 and FWHM2) are significantly decreased when Ni is added 20atm% or more.

Then, time dependence (life characteristic) of electron emitting amount emitted from the carbon
10 fiber of this Example in the same condition as the Example 6 is measured.

As a result, it is possible that all of devices(films) comprising a plurality of carbon fibers formed using the catalytic particles of Pd-Ni
15 alloy show electron emission characteristic near (2) of Fig. 12 shown in the Example 6. And, the catalytic particles having 100% of Ni shows low initial electron emission current density rather than one using catalytic particles of Pd-Ni alloy.
20 On the other hand, the device(film) comprising a plurality of carbon fibers formed using the catalytic particles having 100% of Pd shows electron emission characteristic equal to (1) of Fig. 12 shown in the Example 6. From those results, it is determined that
25 an effective range of Ni addition is 20atm% to 80atm%.
<Example 11>

In this example, growth temperature of carbon

fiber in the example 9 is changed from 580°C to 630°C. Others are identical to the ninth embodiment. Its results are shown in Table 4.

5 (Table 4)

| atm% \ | h1 relative value | h2 relative value | h3 relative value | FWHM1 Kaiser | FWHM2 Kaiser |
|--------------|-------------------------|-------------------------|-------------------------|-----------------|-----------------|
| Pd-Co 20% | 52 | 79 | 12 | 60 | 73 |
| Pd-Co 50% | 52 | 110 | 7 | 49 | 57 |
| Pd-Co 80% | 52 | 105 | 7 | 49 | 50 |

And, though growth of a test piece having 100% of Co is not checked at this growth temperature, growth of carbon fiber is very slow, compared with the case that particles of Pd-Co alloy are used. In addition, it is found that the FWHM s (FWHM1 and FWHM2) are significantly decreased when Co is added in range of 20atm% or more.

Then, time dependence (life characteristic) of electron emission amount emitted from the film containing the carbon fibers of this example is measured in the same condition as the Example 6.

As a result, it is possible that all of devices comprising a plurality of carbon fibers formed using the catalytic particles of Pd-Co alloy show electron emission characteristic near (3) of Fig. 12 shown in the Example 6. And, the catalytic particles having

100% of Co shows lower initial electron emission current density than one using catalytic particles of Pd-Co alloy. On the other hand, the device(film) comprising a plurality of carbon fibers formed using the catalytic particles having 100% of Pd shows electron emission characteristic substantially equal to (1) of Fig. 12 shown in the Example 6. From those results, it is determined that an effective range of Co addition is 20atm% to 80atm%.

10 <Example 12>

A result that Fe is added to Pd in same manner as the Example 8 is shown in Table 5. Method of making catalyst and growth condition of carbon fiber are identical to the Example 9.

15

(Table 5)

| atm% \ | h1 relative value | h2 relative value | h3 relative value | FWHM1 kaiser | FWHM2 kaiser | film thickness μm |
|--------------|-------------------------|-------------------------|-------------------------|-----------------|-----------------|-------------------------|
| Pd-Fe 20% | 52 | 34 | 46 | >120 | >200 | ~3 |
| Pd-Fe 50% | 52 | 27 | 49 | 117 | 192 | ~1 |
| Pd-Fe 80% | 52 | 21 | 52 | 95 | 144 | ~1 |

And, in a test piece having 100% of Fe, growth is not checked at this growth temperature. In addition, it is found that the FWHM s (FWHM1 and FWHM2) are significantly decreased when Fe is added in range of 20atm% or more.

Then, time dependence (life characteristic) of electron emission amount emitted from the film comprising the carbon fibers of Example in the same condition as the Example 6 is measured.

5 As a result, all of devices(films) comprising a plurality of carbon fibers formed using the catalytic particles of Pd-Fe alloy show electron emission characteristic near (2) of Fig. 12 shown in the Example 6, but worse than the electron emitting
10 element ((3) in Fig. 12) prepared in the Example 8. From those results, it is determined that an effective range of Fe addition is 20atm% to 80atm%.
 <Example 12>

 In this Example, a plurality of electron
15 emitting devices having a shape shown in Fig. 2 are prepared using the film containing a plurality of carbon fibers (graphite nanofibers) prepared in the Example 6 (as shown in (c) of Fig. 12), and these are arranged in matrix as shown in Fig. 5 to make the
20 image display device shown in Fig. 6. At this time, a gap between the face plate 710 and the electron source substrate 701 is set to be 2mm. As a result of applying 10kV to the anode 707 of this image display device to display TV image, it is possible to
25 obtain stable image with high brightness for a long time.

(Effects of the Present Invention)

As described above, the catalyst of the present invention enables to provide carbon fiber applicable to an electron emitting element, which excellently grows at a relatively low temperature without needing
5 complex process for stable growth of the carbon fiber at a low temperature. And, since it can be made at a low temperature, the catalyst of the present invention is preferred in aspect of effect on other members and manufacturing costs. In addition, there
10 is no need of explosion-proof equipments for the manufacturing device because there is no danger of fume explosion.

Furthermore, it is possible to prevent deformation of particles being bigger than their
15 initial state when using only Pd, so thus being capable of preventing increase of growth temperature of the carbon fiber and increase of the threshold of electron emission.

And, the present invention enables to obtain
20 stable and excellent electron emitting characteristics for a long time.

WHAT IS CLAIMED IS:

1. An electron emitting device comprising:
a film containing a plurality of carbon fibers,
wherein the film, according to Raman spectrum
5 characteristic detected by irradiating laser having
a wavelength of 514.5nm, has a first peak of
intensity of Raman scattering in which Raman shift
is in a range of $1355 \pm 10 \text{ kaiser}(\text{cm}^{-1})$ and a second
peak of intensity of Raman scattering in which Raman
10 shift is in a range of $1580 \pm 10 \text{ kaiser}$, and
wherein Full-Width Half-Maximum(FWHM2) of the
first peak and a Full-Width Half-Maximum(FWHM1) of
the second peak satisfy a relation that $\text{FWHM2}/\text{FWHM1} \leq$
1.2.
15
2. An electron emitting device comprising:
a film containing a plurality of carbon fibers,
wherein the film, according to Raman spectrum
characteristic detected by irradiating laser having
20 a wavelength of 514.5nm, has a first peak of
intensity of Raman scattering in which Raman shift
is in a range of $1355 \pm 10 \text{ kaiser}(\text{cm}^{-1})$ and a second
peak of intensity of Raman scattering in which Raman
shift is in a range of $1580 \pm 10 \text{ kaiser}$, and
25 wherein a relative intensity h_2 , which is
difference between background intensity and intensity
of the Raman scattering at the first peak, and a

relative intensity h_1 , which is difference between background intensity and intensity of the Raman scattering at the second peak, satisfy a relation that $1.3 \leq h_2/h_1$.

5

3. An electron emitting device comprising:
a film containing a plurality of carbon fibers,
wherein the film, according to Raman spectrum
characteristic detected by irradiating laser having a
10 wavelength of 514.5nm, has a first peak of intensity
of Raman scattering in which Raman shift is in a
range of $1355 \pm 10 \text{ kaiser}(\text{cm}^{-1})$ and a second peak of
intensity of Raman scattering in which Raman shift
is in a range of $1580 \pm 10 \text{ kaiser}$,

15 wherein a Full-Width Half-Maximum (FWHM2) of
the first peak and a Full-Width Half-Maximum (FWHM1)
of the second peak satisfy a relation that
 $\text{FWHM2}/\text{FWHM1} \leq 1.2$, and

20 wherein a relative intensity h_2 , which is
difference between background intensity and intensity
of the Raman scattering at the first peak, and a
relative intensity h_1 , which is difference between
background intensity and intensity of the Raman
scattering at the second peak, satisfy a relation
25 that $1.3 \leq h_2/h_1$.

4. The electron emitting device according to

claim 3,

wherein the relative intensity h_2 and the relative intensity h_1 have a relation that $h_2/h_1 \leq 2.5$.

5

5. The electron emitting device according to any of claims 1 to 3,

wherein a relative intensity h_3 , which is difference between background intensity and minimum intensity of Raman scattering intensity between the first peak and the second peak, is $1/10$ or lower of the relative intensity h_2 , which is difference between background intensity and intensity of Raman scattering at the first peak.

15

6. The electron emitting device according to claim 5,

wherein the relative intensity h_3 is $1/15$ or lower of the relative intensity h_2 .

20

7. The electron emitting device according to any of claims 1 to 3,

wherein the carbon fiber is graphite nanofiber having graphenes laminated not in parallel to the axial direction thereof.

25

8. The electron emitting device according to

any of claims 1 to 3,

wherein the plurality of carbon fibers included in the film containing a plurality of carbon fibers have density of $10^3/\text{cm}^2$ or more.

5

9. The electron emitting device according to any of claims 1 to 3,

wherein the number of electron emission sites of the film containing a plurality of carbon fibers is $10^3/\text{cm}$ or more when electric field intensity $1 \times 10^5\text{V}/\text{cm}$ or more is applied to the film containing a plurality of carbon fiber.

10. An electron emitting device comprising:
15 a film containing a plurality of carbon fibers, wherein the carbon fiber is graphite nanofiber having graphenes laminated not in parallel to the axial direction thereof, and

wherein the plurality of carbon fibers included
20 in the film containing a plurality of carbon fibers have density of $10^3/\text{cm}^2$ or more.

11. The electron emitting device according to any of claims 1 to 3 and 10, further comprising a
25 gate electrode and a cathode electrode positioned on a surface of a substrate with a space therebetween, wherein the film containing a plurality of

carbon fibers is disposed on the cathode electrode to be electrically connected thereto, and at least a part of a surface of the film containing a plurality of carbon fibers is positioned on the surface of the substrate to be spaced apart more than a distance between a surface of the gate electrode and the surface of the substrate.

12. The electron emitting device according to claim 11,

wherein the cathode electrode has metallic nitride on at least the surface thereof.

13. The electron emitting device according to claim 12,

wherein the metallic nitride is TiN.

14. An electron source having a plurality of electron emitting devices, wherein the electron emitting device is one defined in any of claims 1 to 3 and 10.

15. An image display device including an electron source and a member, which emits light when electrons are irradiated thereto,

wherein the electron source is one defined in claim 14.

16. An image display device comprising:

a first substrate on which an electron emitting device having a film containing a plurality of carbon fibers is arranged, and a second substrate having a light emitting member and an anode electrode and arranged in opposition to the first substrate, wherein the carbon fiber is graphite nanofiber having graphenes laminated not in parallel to the axial direction thereof,

wherein the number of electron emission sites of the film containing a plurality of carbon fibers is $10^3/\text{cm}$ or more when electrons are emitted from the film containing a plurality of carbon fibers by electric field intensity $1 \times 10^5 \text{V/cm}$ or more is applied between the film containing a plurality of carbon fiber and the anode electrode.

17. A catalyst used to form carbon fiber, which contains Pd and at least one element selected in the group consisting of Fe, Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu,

wherein 20atm% or more (atomic percentage) of the selected at least one element is contained to Pd.

18. The catalyst used to form carbon fiber according to claim 17,

wherein 80atm% or less (atomic percentage) of

the selected at least one element is contained to Pd.

19. The catalyst used to form carbon fiber according to claim 17,

5 wherein the catalyst is in a particle state, and Pd and the selected at least one element are included in an alloy state.

20. The catalyst used to form carbon fiber according to claim 17,

wherein the carbon fiber is graphite nanofiber having graphenes laminated not in parallel to the axial direction thereof.

15 21. A catalyst used to form carbon fiber, which contains Pd and at least one element selected in the group consisting of Fe, Co and Ni,

wherein 20atm% or more (atomic percentage) of the selected at least one element is contained to Pd.
20

22. The catalyst used to form carbon fiber according to claim 21,

wherein less than 80atm% or lower (atomic percentage) of the selected at least one element is
25 contained to Pd.

23. The catalyst used to form carbon fiber

according to claim 21,

wherein the catalyst is in a particle state,
and Pd and the selected at least one element are
included in an alloy state.

5

24. The catalyst used to form carbon fiber
according to claim 21,

wherein the carbon fiber is graphite nanofiber
having graphenes laminated not in parallel to the
10 axial direction thereof.

25. A method of making a film containing a
plurality of carbon fibers comprising the steps of:

arranging a catalyst on a substrate; and
15 heat-treating the substrate on which the
catalyst is arranged under circumstance including
hydrocarbon gas and hydrogen,

wherein the catalyst contains Pd and at least
one element selected in the group consisting of Fe,
20 Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er
and Lu, and 20atm% or more (atomic percentage) of the
selected at least one element is contained to Pd.

26. A method of making a film containing a
25 plurality of carbon fibers comprising the steps of:

arranging a plurality of catalytic particles on
a substrate; and

heat-treating the substrate on which the plurality of catalytic particles are arranged under circumstance including hydrocarbon gas and hydrogen, wherein the catalyst contains Pd and at least

5 one element selected in the group consisting of Fe, Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu, and 20atm% or more (atomic percentage) of the selected at least one element is contained to Pd.

10 27. A method of making an electron emitting device comprising the steps of:

disposing a film containing metal on a substrate;

15 arranging a plurality of catalytic particles on the film containing metal; and

heat-treating the substrate on which the plurality of catalytic particles are arranged under circumstance including hydrocarbon gas and hydrogen to form a plurality of carbon fibers,

20 wherein the catalyst contains Pd and at least one element selected in the group consisting of Fe, Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu, and 20atm% or more (atomic percentage) of the selected at least one element is contained to Pd.

25 .

28. A method of making an electron emitting device comprising the steps of:

disposing a film containing metal on a substrate;

arranging a plurality of catalytic particles on the film containing metal; and

5 heat-treating the substrate on which the plurality of catalytic particles are arranged under circumstance including hydrocarbon gas and hydrogen to form a plurality of carbon fibers,

 wherein the catalytic particles contains Pd and
10 at least one element selected in the group consisting of Fe, Co and Ni, and 20atm% or more (atomic percentage) of the selected at least one element is contained to Pd.

15 29. The method of making an electron emitting device according to claim 27 or 28,

 wherein the film containing metal has metallic nitride at least on a surface thereof.

20 30. The method of making an electron emitting device according to claim 29,

 wherein the metallic nitride is TiN.

 31. A method of making an electron source
25 having a plurality of electron emitting devices,

 wherein the electron emitting device made by the method defined in claim 27 or 28.

32. A method of making an image forming apparatus having an electron source and an image forming member,

wherein the electron source is made by the
5 method defined in claim 29.

33. A method of making a catalyst, which makes the catalyst defined in claim 17 by vacuum evaporation in which Pd is set as a first evaporation
10 source for vacuum evaporation and at least one selected in the group consisting of Fe, Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu is set as a second evaporation source for vacuum evaporation.

15 34. A method of making a catalyst according to claim 33,

wherein the vacuum evaporation uses a sputtering manner.

20 35. A method of making a catalyst, which makes the catalyst defined in claim 17 by coating mixed liquid of a first liquid containing Pd and a second liquid containing at least one selected in the group consisting of Fe, Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd,
25 Gd, Tb, Dy, Ho, Er and Lu on a substrate.

36. A cathode of a secondary battery
containing a plurality of carbon fibers,

wherein a film containing a plurality of the
carbon fibers, according to Raman spectrum
5 characteristic detected by irradiating laser having a
wavelength of 514.5nm, has a first peak of intensity
of Raman scattering in which Raman shift is in a
range of $1355 \pm 10\text{kaiser}(\text{cm}^{-1})$ and a second peak of
intensity of Raman scattering in which Raman shift
10 is in a range of $1580 \pm 10\text{kaiser}$, and

wherein a Full-Width Half-Maximum (FWHM2) of
the first peak and a Full-Width Half-Maximum (FWHM1)
of the second peak satisfy a relation that
 $\text{FWHM2}/\text{FWHM1} \leq 1.2$.

15

37. A cathode of a secondary battery
containing a plurality of carbon fibers,

wherein a film containing a plurality of the
carbon fibers, according to Raman spectrum
20 characteristic detected by irradiating laser having a
wavelength of 514.5nm, has a first peak of intensity
of Raman scattering in which Raman shift is in a
range of $1355 \pm 10\text{kaiser}(\text{cm}^{-1})$ and a second peak of
intensity of Raman scattering in which Raman shift
25 is in a range of $1580 \pm 10\text{kaiser}$, and

wherein a relative intensity h_2 , which is
difference between background intensity and intensity

of the Raman scattering at the first peak, and a relative intensity h_1 , which is difference between background intensity and intensity of the Raman scattering at the second peak, satisfy a relation
5 that $1.3 \leq h_2/h_1$.

38. A cathode of a secondary battery containing a plurality of carbon fibers,
wherein the plurality of carbon fibers,
10 according to Raman spectrum characteristic detected by irradiating laser having a wavelength of 514.5nm, has a first peak of intensity of Raman scattering in which Raman shift is in a range of $1355 \pm$
10kaiser(cm^{-1}) and a second peak of intensity of Raman
15 scattering in which Raman shift is in a range of $1580 \pm 10\text{kaiser}$,

wherein a Full-Width Half-Maximum (FWHM2) of the first peak and a Full-Width Half-Maximum (FWHM1) of the second peak satisfy a relation that
20 $\text{FWHM2}/\text{FWHM1} \leq 1.2$, and wherein a relative intensity h_2 , which is difference between background intensity and intensity of the Raman scattering at the first peak, and a relative intensity h_1 , which is
difference between background intensity and intensity
25 of the Raman scattering at the second peak, satisfy a relation that $1.3 \leq h_2/h_1$.

39. A body for a hydrogen storing, containing a plurality of carbon fibers,

wherein the plurality of carbon fibers, according to Raman spectrum characteristic detected
5 by irradiating laser having a wavelength of 514.5nm, has a first peak of intensity of Raman scattering in which Raman shift is in a range of $1355 \pm 10\text{kaiser}(\text{cm}^{-1})$ and a second peak of intensity of Raman scattering in which Raman shift is in a range of
10 $1580 \pm 10\text{kaiser}$, and

wherein a Full-Width Half-Maximum (FWHM2) of the first peak and a Full-Width Half-Maximum (FWHM1) of the second peak satisfy a relation that $\text{FWHM2}/\text{FWHM1} \leq 1.2$.

15

40. A body for a hydrogen storing, containing a plurality of carbon fibers,

wherein the plurality of carbon fibers, according to Raman spectrum characteristic detected
20 by irradiating laser having a wavelength of 514.5nm, has a first peak of intensity of Raman scattering in which Raman shift is in a range of $1355 \pm 10\text{kaiser}(\text{cm}^{-1})$ and a second peak of intensity of Raman scattering in which Raman shift is in a range of
25 $1580 \pm 10\text{kaiser}$, and

wherein a relative intensity h_2 , which is difference between background intensity and intensity

of the Raman scattering at the first peak, and a relative intensity h_1 , which is difference between background intensity and intensity of the Raman scattering at the second peak, satisfy a relation
5 that $1.3 \leq h_2/h_1$.

41. A body for a hydrogen storing, containing a plurality of carbon fibers,

wherein the plurality of carbon fibers,
10 according to Raman spectrum characteristic detected by irradiating laser having a wavelength of 514.5nm, has a first peak of intensity of Raman scattering in which Raman shift is in a range of $1355 \pm 10\text{kaiser}(\text{cm}^{-1})$ and a second peak of intensity of Raman
15 scattering in which Raman shift is in a range of $1580 \pm 10\text{kaiser}$,

wherein a Full-Width Half-Maximum (FWHM2) of the first peak and a Full-Width Half-Maximum (FWHM1) of the second peak satisfy a relation that
20 $\text{FWHM2}/\text{FWHM1} \leq 1.2$, and

wherein a relative intensity h_2 , which is difference between background intensity and intensity of the Raman scattering at the first peak, and a relative intensity h_1 , which is difference between
25 background intensity and intensity of the Raman scattering at the second peak, satisfy a relation that $1.3 \leq h_2/h_1$.

ABSTRACT OF THE DISCLOSURE

A catalyst for promoting growth of carbon fiber, which is capable of growing satisfactorily at a low temperature without needing complex process and
5 applicable to such as electron emitting device.

The catalyst used for growth of carbon fiber contains Pd and at least one element selected in the group consisting of Fe, Co, Ni, Y, Rh, Pt, La, Ce, Pr, Nd, Gd, Tb, Dy, Ho, Er and Lu, in which 20~80atm%
10 (atomic percentage) of the selected at least one element is contained to Pd.

FIG. 1A

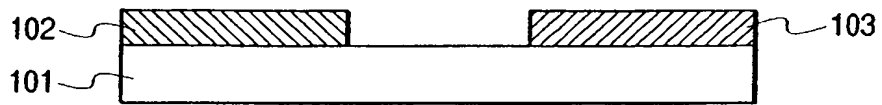


FIG. 1B

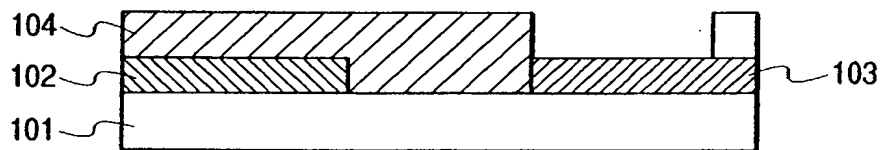


FIG. 1C

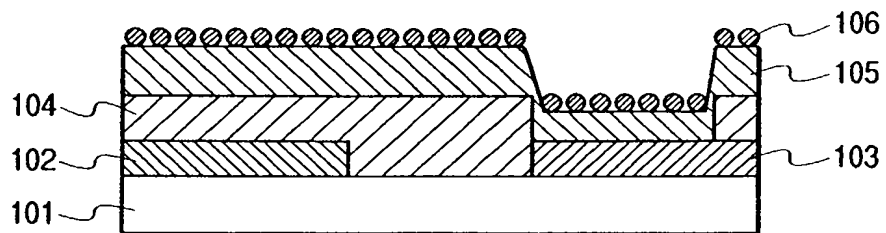


FIG. 1D

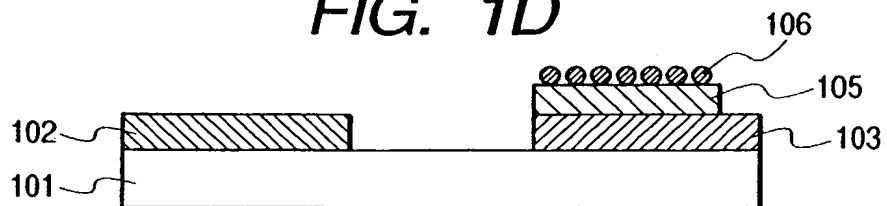


FIG. 1E

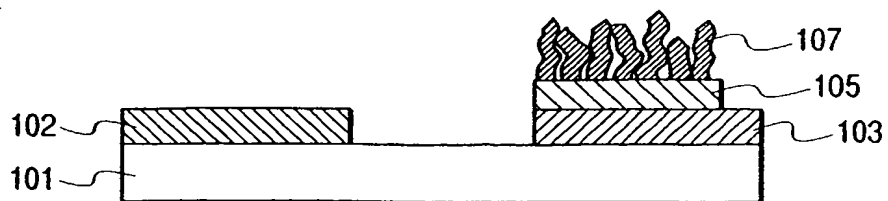


FIG. 2A

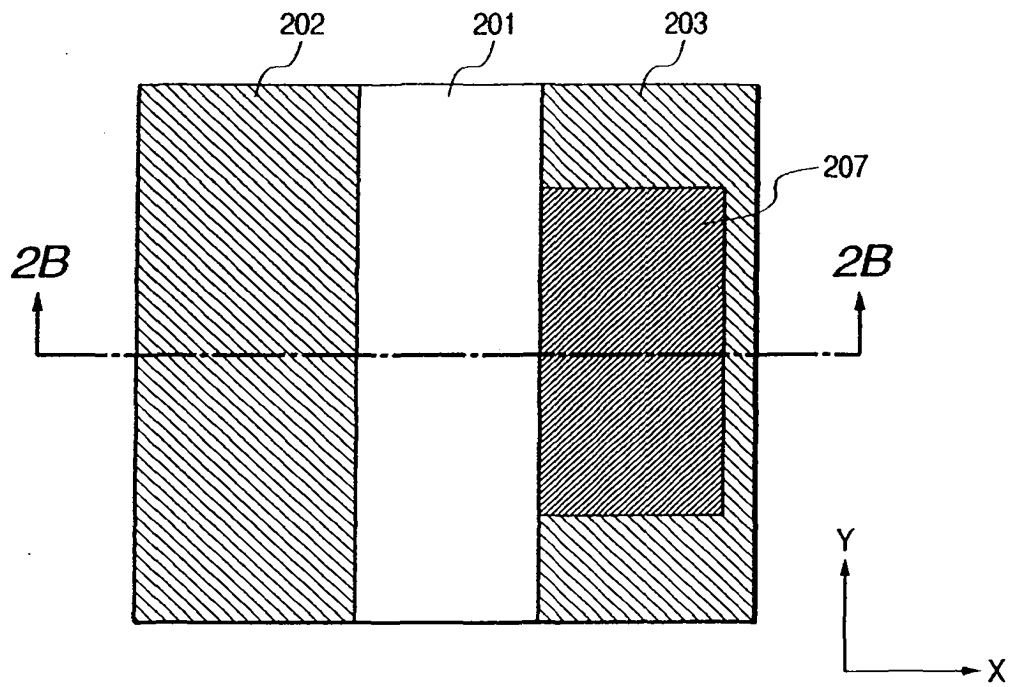


FIG. 2B

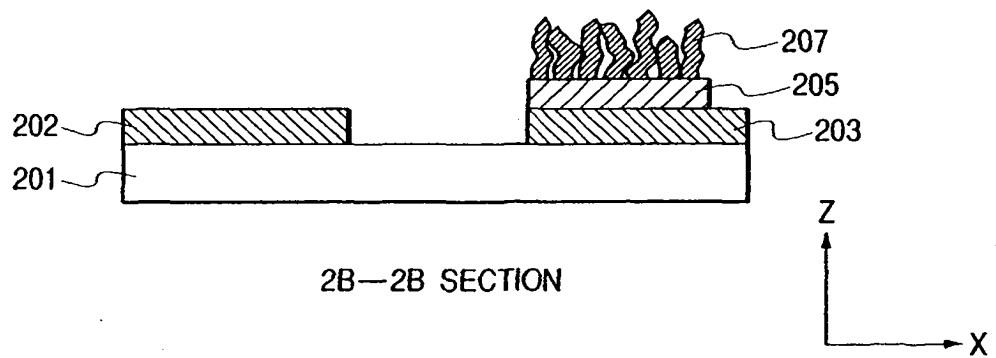


FIG. 3

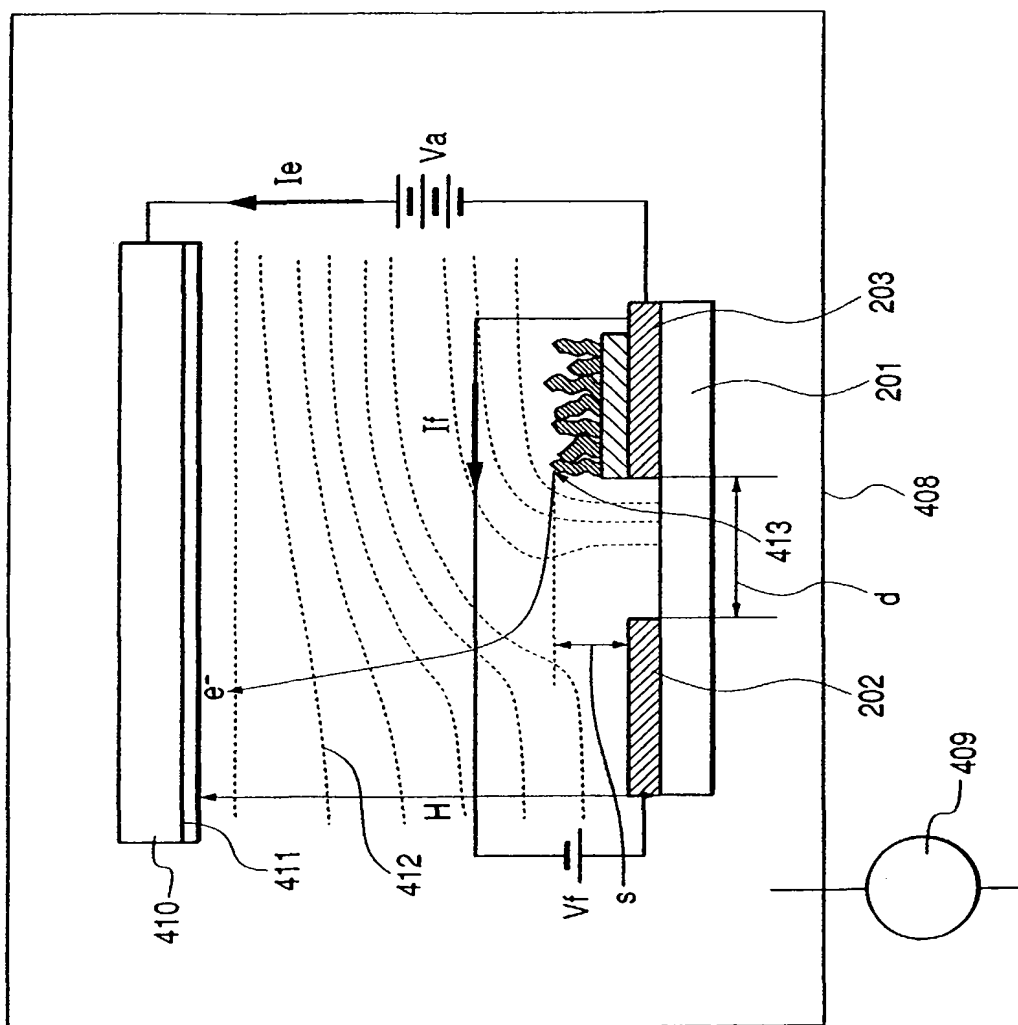


FIG. 4

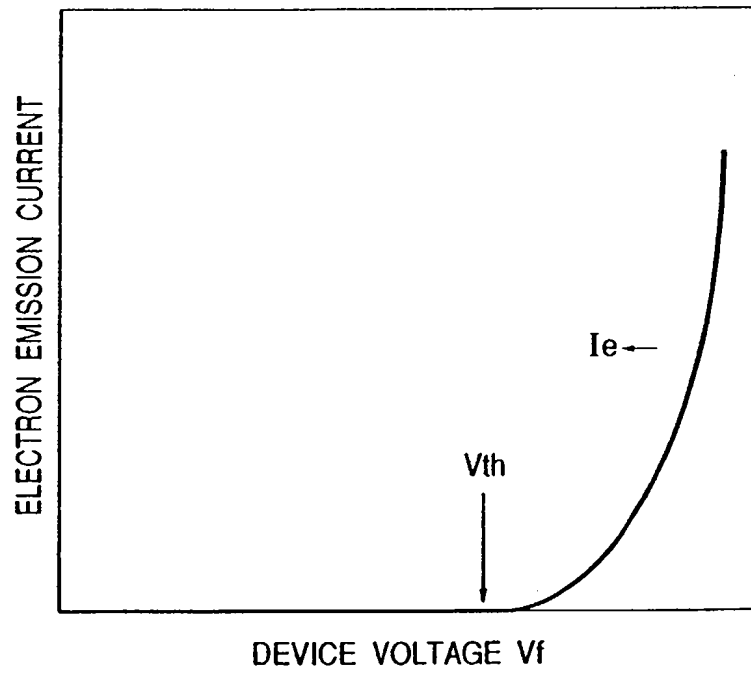


FIG. 5

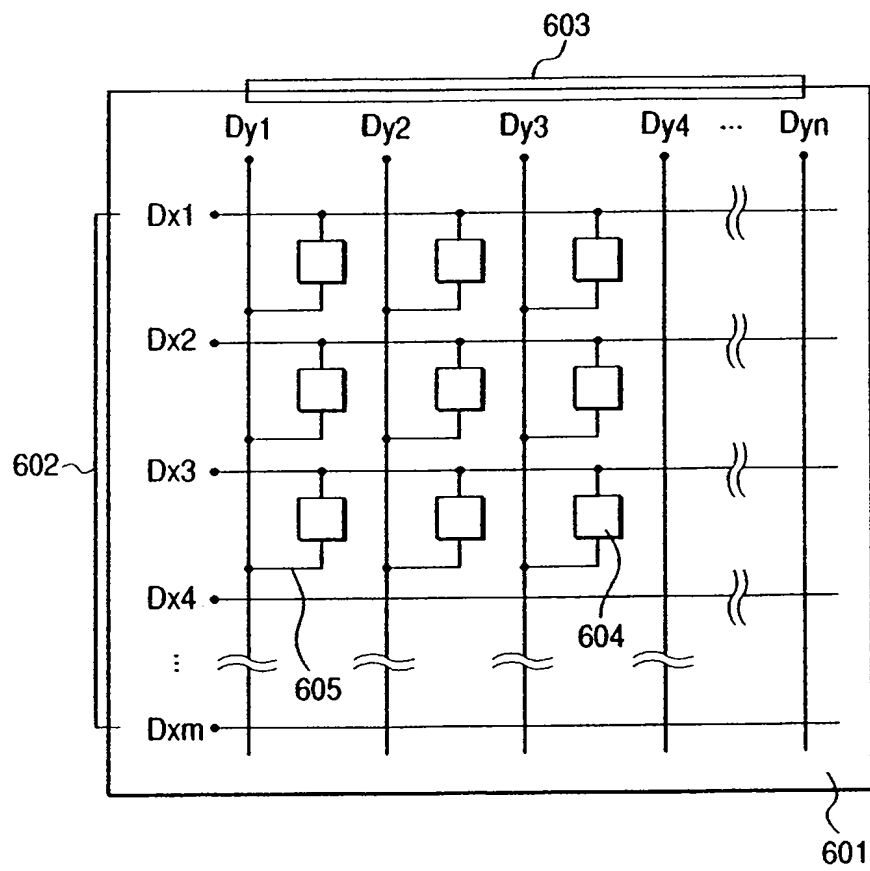


FIG. 6

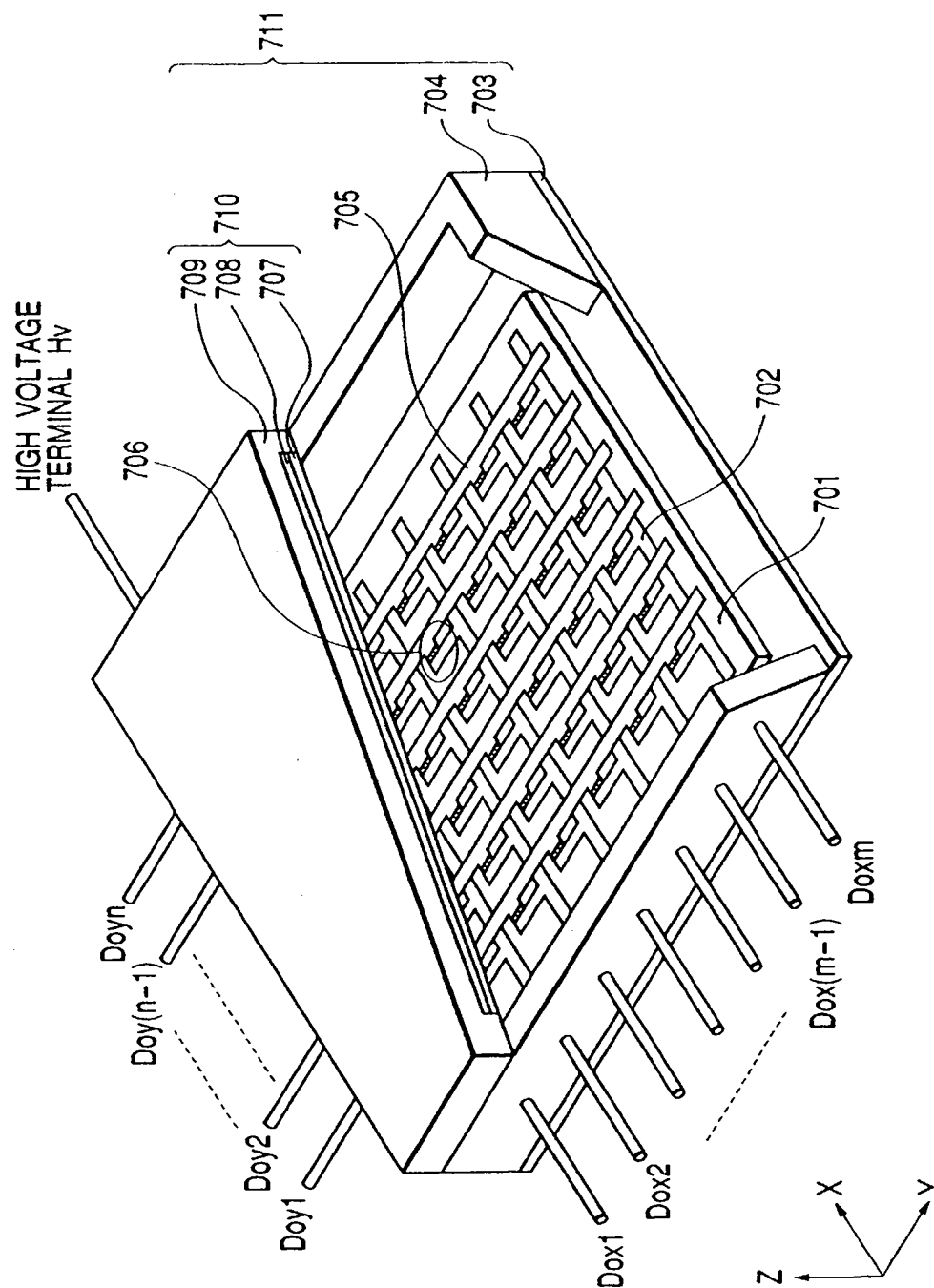


FIG. 7

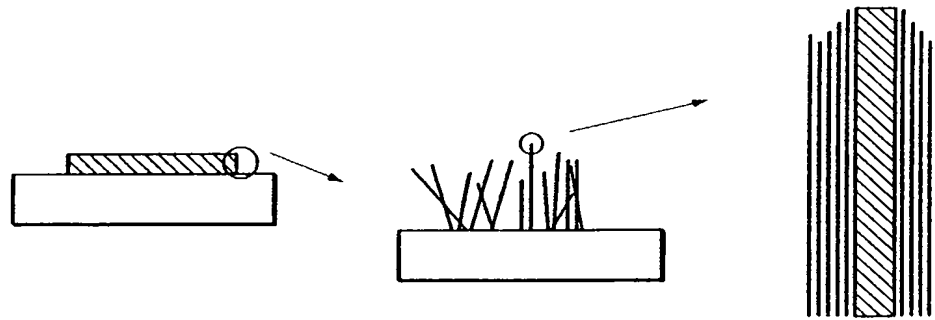


FIG. 8

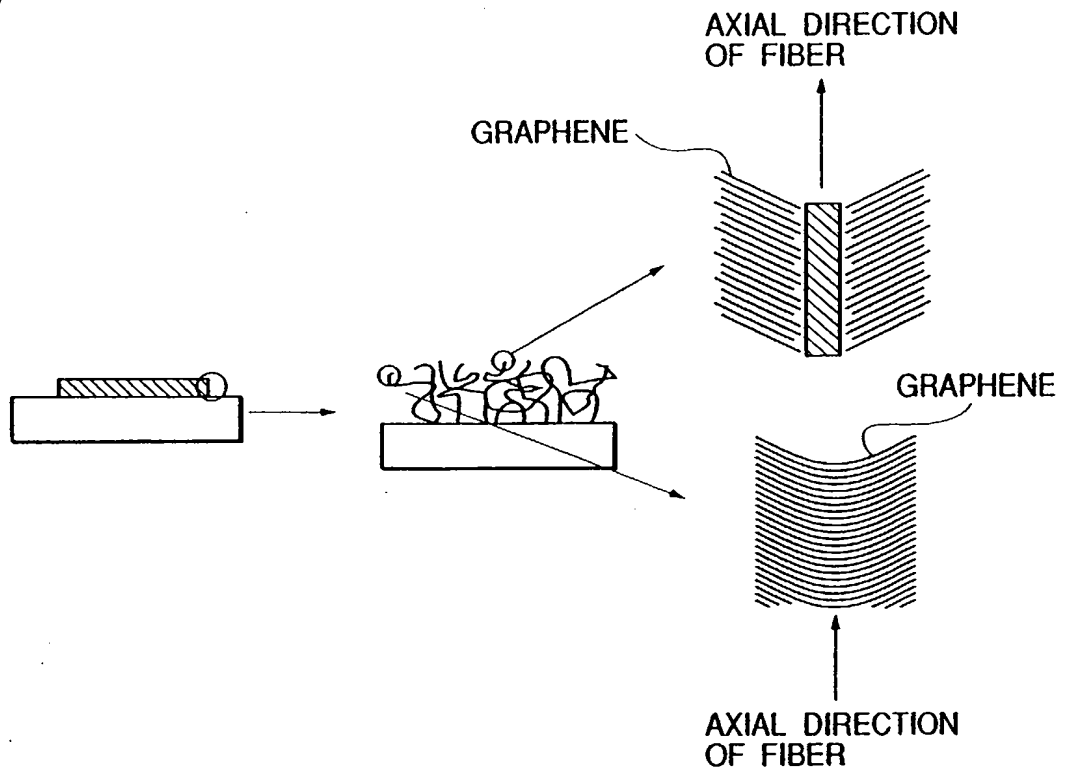


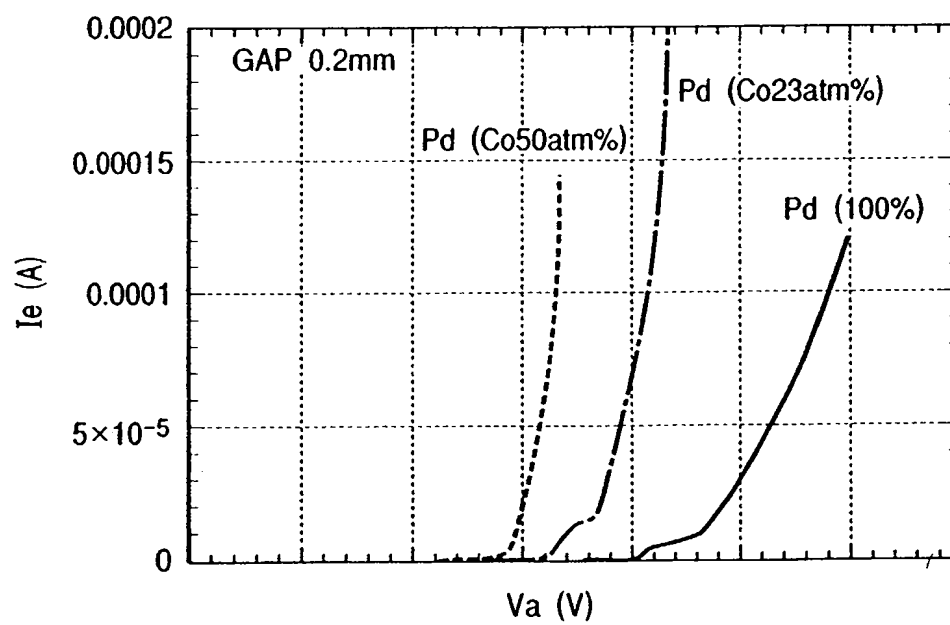
FIG. 9

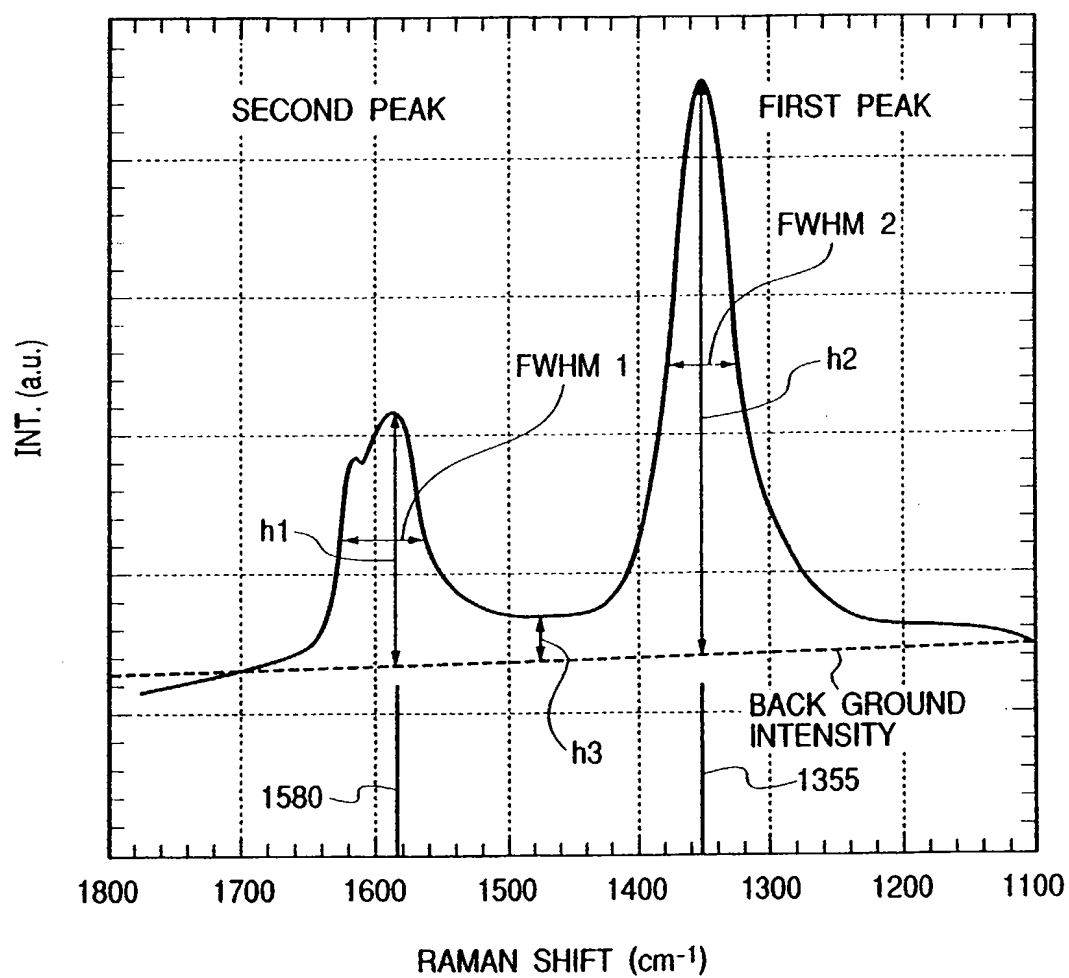
FIG. 10

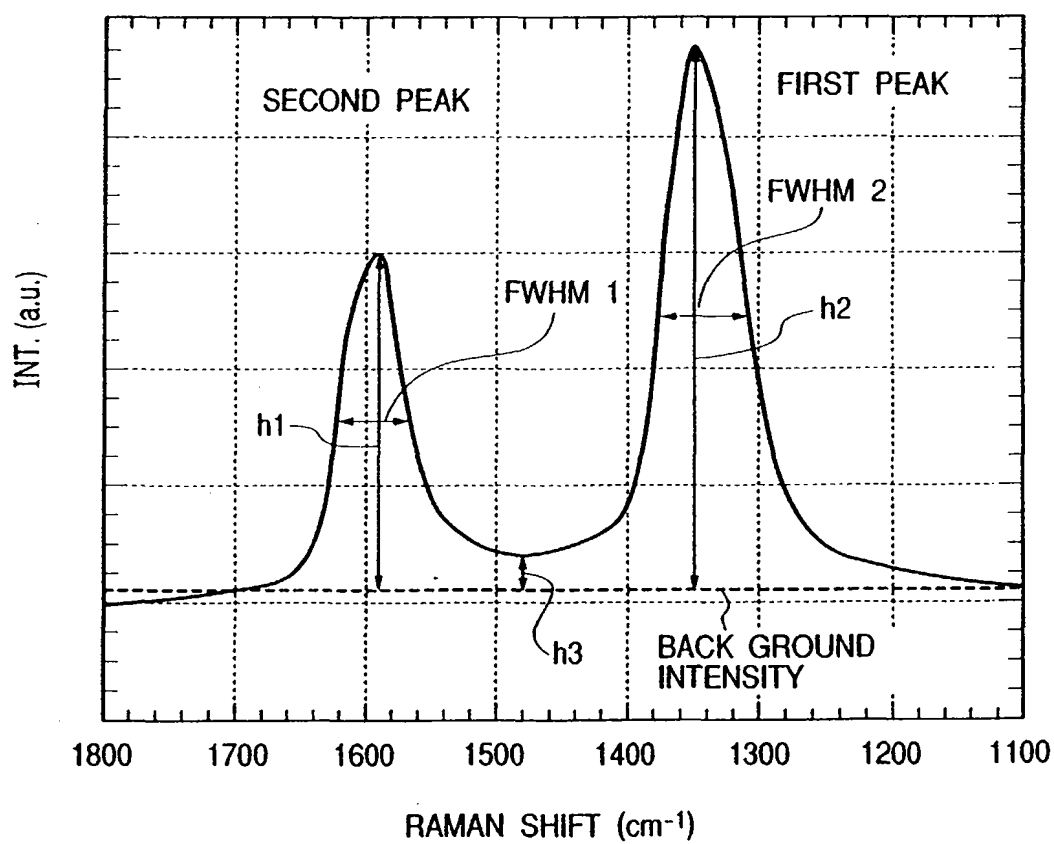
FIG. 11

FIG. 12

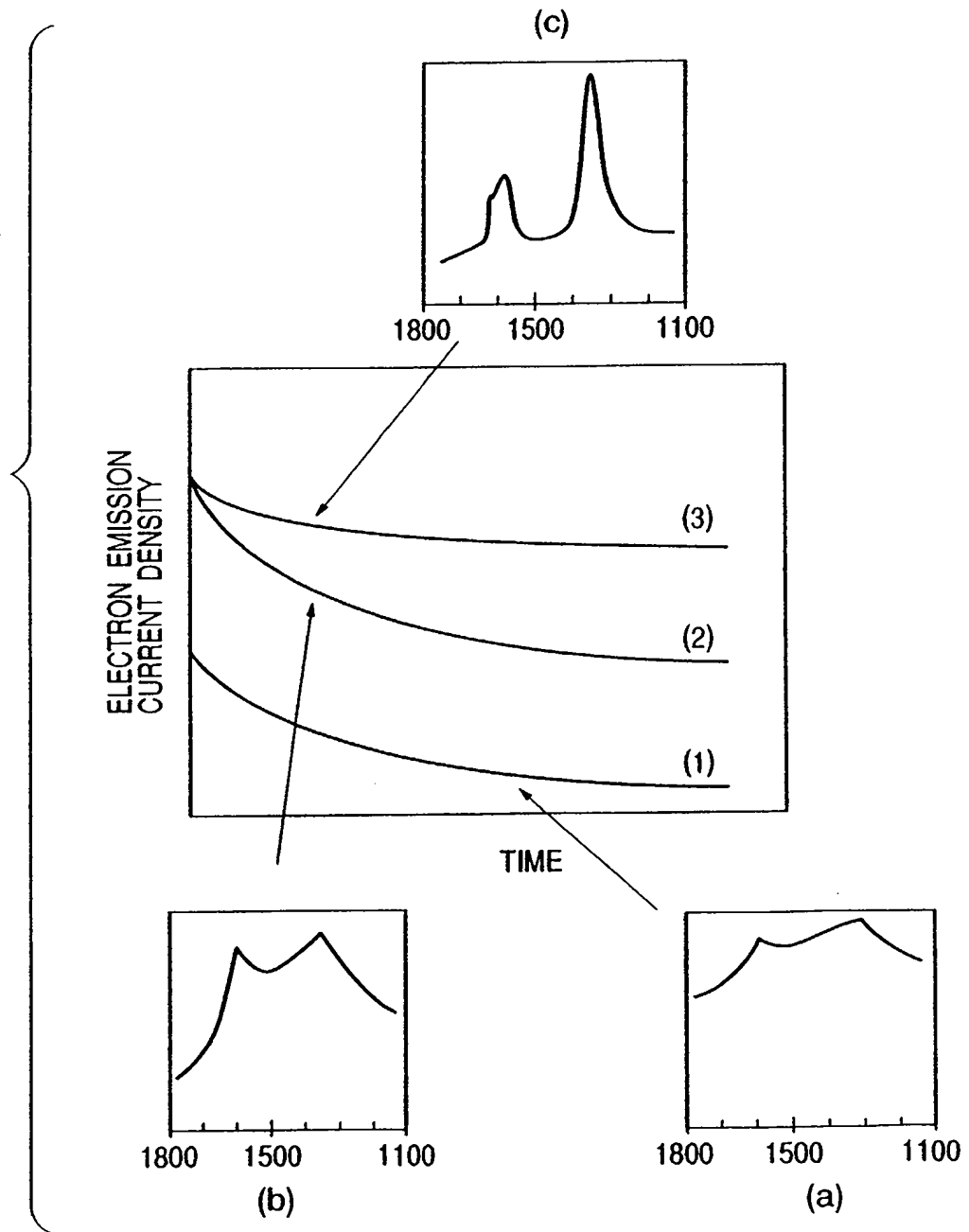


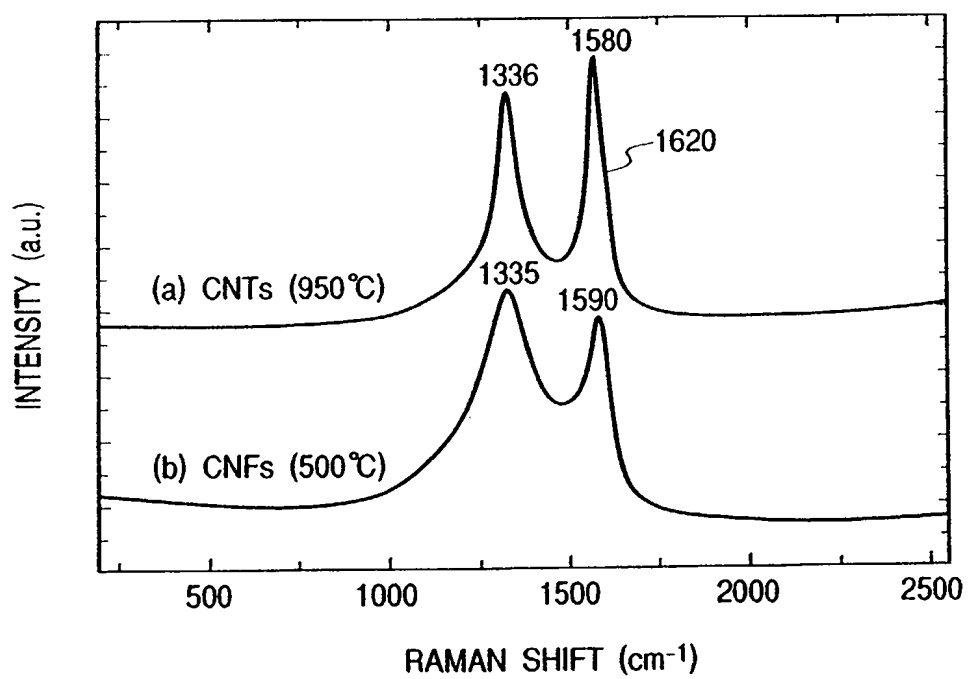
FIG. 13

FIG. 14

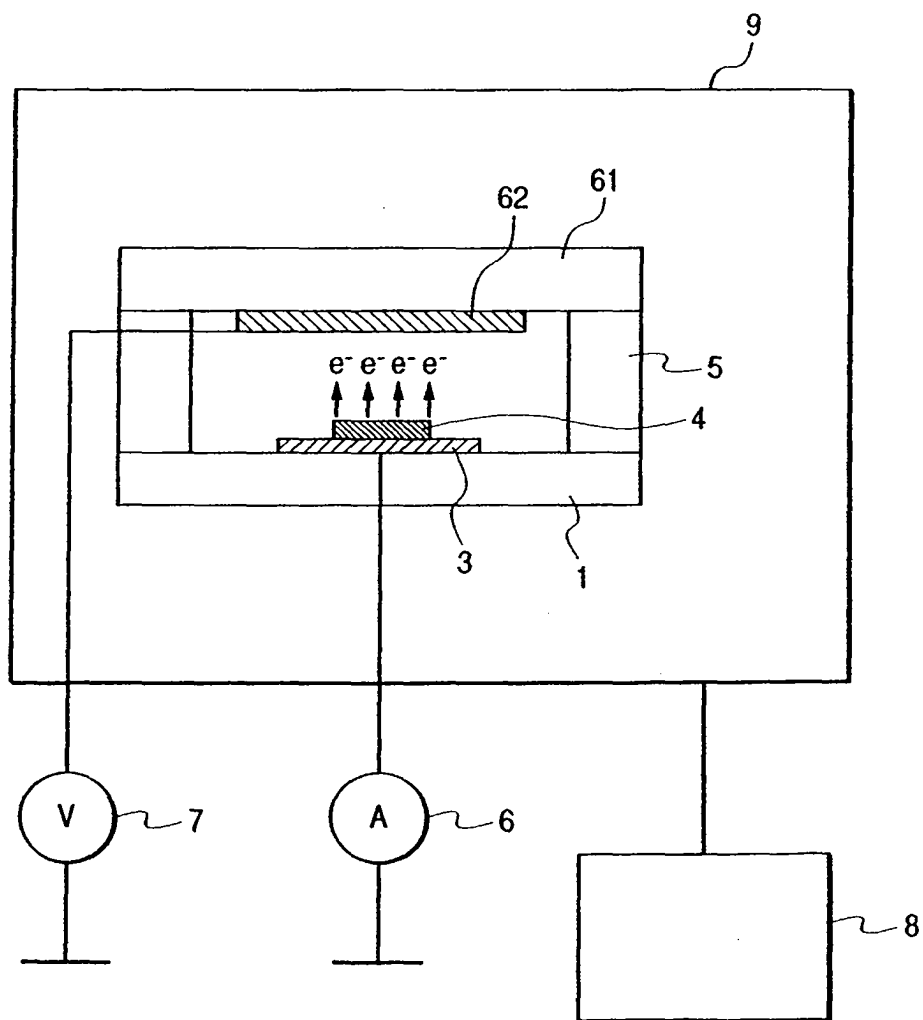


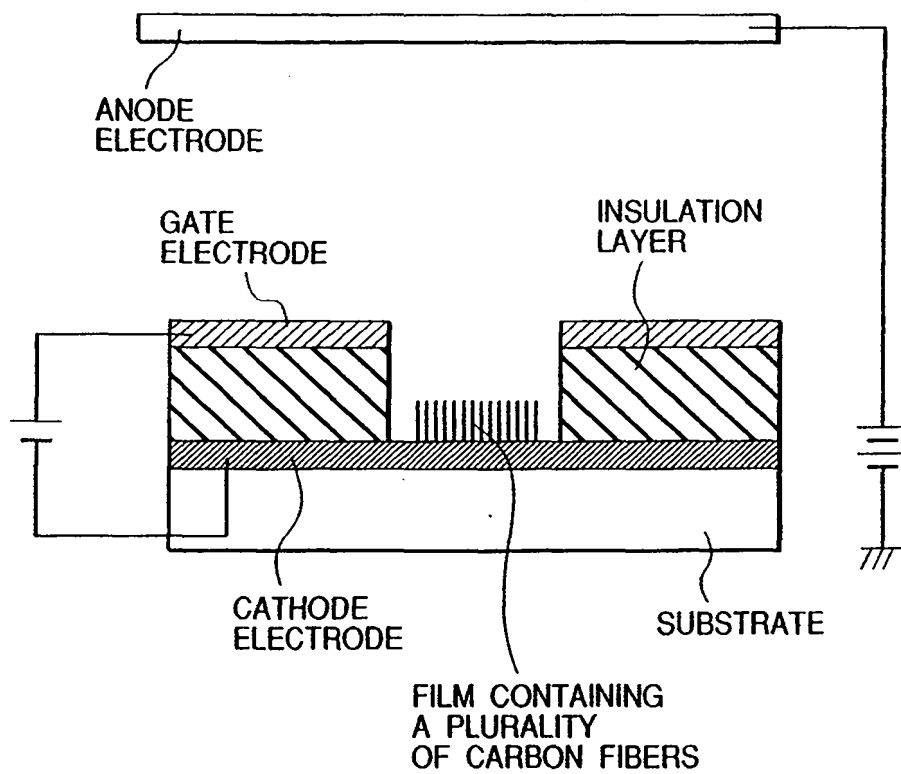
FIG. 15

FIG. 16A

FIG. 16B

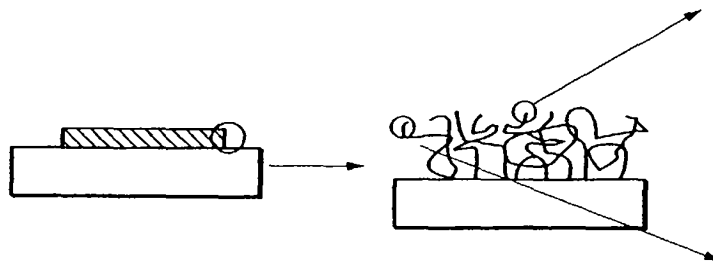
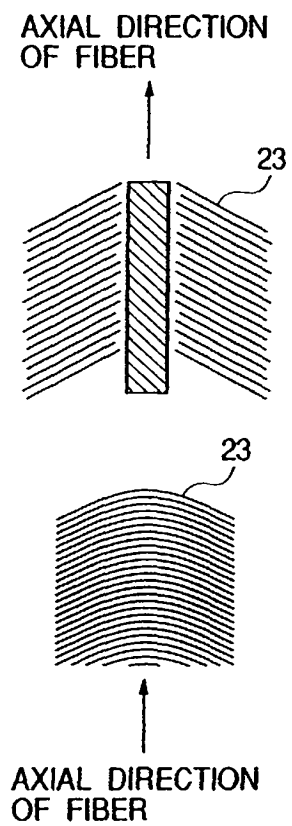


FIG. 16C



The attached application:

U.S. Application No.: 10/234,213
Filing Date: 9-5-02
Group Art Unit: 2879

is part of an IDS filed in U.S. Application No.: 07/941,595

- 1 -

CFO 16705 US
10/234,213
9-5-02
044 2879

MANUFACTURE METHOD FOR ELECTRON-EMITTING DEVICE,
ELECTRON SOURCE, LIGHT-EMITTING APPARATUS, AND IMAGE
FORMING APPARATUS

5 BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a method of manufacturing electron-emitting devices, electron sources, light-emitting apparatuses and image forming
10 apparatuses. Image forming apparatuses may be display apparatuses for television broadcasting, display apparatuses for television conference systems and computers and the like, optical printers using photosensitive drums and the like.

15 Related Background Art

Two types of electron emitting-devices are known, thermionic cathode devices and cold cathode devices. Known cold cathode devices include field emission devices, metal/insulator/metal emission
20 devices, and surface conduction electron-emitting devices. Image forming apparatuses using electron-emitting devices are required nowadays to have a high resolution. As the number of display pixels increases, a consumption power increases because of
25 capacitances of electron-emitting devices being driven. It is therefore desired to reduce device capacitance, lower drive voltage and improve the

efficiency of electron-emitting devices. It is also required that the electron emission characteristics of electron-emitting devices are uniform and devices can be easily manufactured. Recently, many proposals
5 have been made to use carbon nanotubes as electron-emitting devices, carbon nanotubes being expected to meet such requirements.

Manufacturing and patterning methods for electron-emitting devices using carbon nanotubes have
10 been proposed in various ways (as disclosed in Japanese Patent Laid-Open Application No. 11-162334, No. 2000-057934, No. 2000-086216, No. 2000-090809, U.S. Patent No. 6290564, etc.). For example, by using resist, a dot pattern is formed in a substrate
15 to dispose catalyst metal at desired positions and grow carbon nanotubes by using the catalyst metal as nuclei (JP-A-2000-086216). Assistants are attached to a substrate and carbon nanotubes are formed at desired positions of the substrate by plasma CVD in
20 an electric field (JP-A-2000-057934). Carbon nanotubes are manufactured by arc discharge or by laser radiation to graphite and refined. Thereafter, the carbon nanotubes are dispersed in solution or resist liquid and this dispersion liquid is coated on a
25 substrate (JP-A-2000-90809).

SUMMARY OF THE INVENTION

The device manufacture method which grows carbon nanotubes by using catalyst as nuclei requires a plurality of complicated processes because it is necessary to fix a metal catalyst to a substrate at
5 proper size, proper particle diameter and proper pitch.

The device manufacture method which coats liquid dispersed with carbon nanotubes as described in JP-A-2000-90809 has an increased number of
10 processes and requires a high cost because it is necessary to pattern the dispersion liquid in only desired areas of a substrate and to perform a post-process like a baking process.

The device manufacture method which uses
15 adhesive as described in JP-A-11-162334 inevitably increases the number of processes because it is necessary to coat adhesive before disposing a plurality of a columnar graphite and perform a baking process after the disposing.

20 An object of the invention is to provide a method of manufacturing an electron-emitting device having excellent electron emission characteristics in which fibers comprising carbon as the main composition (as the main ingredients) are directly
25 fixed (bonded) to a substrate (or a electrode disposed on a substrate) in a desired area and at a desired density with simple processes and inexpensive

manufacturing cost, and to provide a manufacturing method for an electron source, a light-emitting apparatus and an image forming apparatus using such electron-emitting devices.

5 Specifically, the invention provides a method of manufacturing an electron-emitting device wherein a material comprising carbon as the main composition (as the main ingredients) is aerosolized and transported together with gas, and tightly attached
10 (bonded) to a substrate via a nozzle.

 The material comprising carbon as the main composition (as the main ingredients) may be fibers comprising carbon as the main composition (as the main ingredients). The fibers comprising carbon as
15 the main composition (as the main ingredients) may be at least ones selected from a group consisting of graphite nanofibers, carbon nanotubes, amorphous carbon fibers and carbon nanohorns.

 The invention provides a method of
20 manufacturing an electron-emitting device, the method comprising: (A) a step of preparing fibers comprising carbon as main composition (as the main ingredients) in a first chamber; (B) a step of disposing a substrate in a second chamber; and (C) a step of
25 colliding the fibers comprising carbon as the main composition (as the main ingredients) with the substrate via a transport tube communicating with the

first and second chamber by setting a pressure in the first chamber higher than a pressure in the second chamber, to fix (bonded) the fibers comprising carbon as the main composition (as the main ingredients) to the substrate.

The substrate on which the carbon fibers are used also as a negative electrode material of a fuel cell, a negative electrode material of a secondary cell and a hydrogen absorbing substance.

10 The fibers comprising carbon as the main composition (as the main ingredients) may be dispersed in gas in the first chamber. The gas may be non-oxidizing gas.

15 The inside of the second chamber may be in a reduced pressure state. The fibers comprising carbon as the main composition (as the main ingredients) may be aerosolized in the first chamber.

20 The fibers comprising carbon as the main composition (as the main ingredients) can be fixed (bonded) to the substrate by heat energy generated when the fibers comprising carbon as the main composition collides with the substrate. The fibers comprising carbon as the main composition may be at least ones selected from a group consisting of
25 graphite nanofibers, carbon nanotubes, amorphous carbon fibers and carbon nanohorns.

A first conductive layer may be disposed on the

substrate and the fibers comprising carbon as the main composition may be fixed (bonded) to the first conductive layer. A second conductive layer may be disposed on the substrate, the second conductive
5 layer being spaced apart from the first conductive layer.

The invention provides a method of manufacturing an electron source comprising a plurality of electron-emitting devices wherein the
10 electron-emitting device is manufactured by the above-described method of the invention.

The invention provides a method of manufacturing an image forming apparatus comprising an electron source and a light emitting member
15 wherein the electron source is manufactured by the above-described method of the invention.

The invention provides a method of manufacturing a light-emitting apparatus comprising electron-emitting devices and light-emitting members
20 wherein the electron-emitting device is manufactured by the above-described method of the invention.

The manufacture method of the invention is not a method of forming catalyst on a substrate and growing fibers comprising carbon as the main
25 composition by using the catalyst as nuclei. As will be later described, the manufacture method of the invention directly fixes fibers comprising carbon as

the main composition to a substrate. More specifically, aerosolized fibers comprising carbon as the main composition are ejected from a nozzle and collide with the substrate in a desired area to fix
5 (bond) the fibers to the desired area of the substrate without using adhesive.

According to the method of the invention, fibers comprising carbon as the main composition are aerosolized and directly ejected toward a substrate
10 together with gas. Therefore, the fibers fixed to the substrate can be disposed at an angle perpendicular to or substantially perpendicular to the substrate surface. Since the fibers can be fixed (bonded) vertically or approximately vertically to
15 the substrate surface. An electric field can be concentrated upon a tip of each sharp fiber so that the electron-emitting device having stable and excellent electron emission characteristics can be manufactured. In the above described invention, it
20 is noted that the fibers used to this invention are not limited to the fibers comprising carbon as the main composition. Therefore, fibers comprising metal (or substance having metallic characteristic) as the main composition can be also used in the invention
25 described above. According to the method of the invention, it is not necessary to heat a substrate to a high temperature in order to grow and fix fibers to

a device substrate as in conventional techniques. It is therefore possible to lower a power consumption and manufacture cost.

5 BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic diagram showing an example of a manufacture system of the invention.

Fig. 2 is a schematic cross sectional view of electrodes formed on a substrate.

10 Fig. 3 is a schematic cross sectional view showing an example of an electron-emitting device of the invention.

Figs. 4A and 4B are a schematic plan view and a schematic cross sectional view showing an example of
15 an electron-emitting device of the invention.

Fig. 5 is a diagram showing the outline structure of an evaluation system for measuring electron emission characteristics.

Figs. 6A, 6B and 6C are schematic diagrams
20 showing an example of fibers comprising carbon as the main composition.

Figs. 7A, 7B and 7C are schematic diagrams showing another example of fibers comprising carbon as the main composition.

25

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the present invention, the phrase "fibers

comprising carbon as the main composition" may be replaced with a phrase "columnar substance comprising carbon as the main composition" or a phrase "linear substance comprising carbon as the main composition".

5 Also in the present invention, the phrase "fibers comprising carbon as the main composition" may be replaced with a phrase "fibrous carbon" or a phrase "carbon fibers". Examples of "fibers comprising carbon as the main composition" are carbon nanotubes,
10 graphite nanofibers, amorphous carbon fibers, carbon nanohorns with one closed end of a carbon nanotube, and mixtures of these. Among these, graphite nanofibers are most suitable.

One plane (sheet) of graphite is called a
15 "graphen" or a "graphen sheet". More specifically, graphite comprises a plurality of stacked or layered carbon planes. Each carbon plane comprises a repeated hexagon having a carbon atom at each vertex thereof and having a covalent bond along each side
20 thereof. The covalent bond is caused by sp² hybrid orbitals of carbon atoms. Ideally, the distance (interval) between the neighboring carbon planes is 3.354×10^{-10} m. Each carbon plane (sheet) is called a "graphen" or a "graphen sheet".

25 Examples of the structure of fibers comprising carbon as the main composition are schematically shown in Figs. 6A to 6C and 7A to 7C. In Figs. 6A to

6C and 7A to 7C, reference numeral 16 represents a graphen. The structure of fibers as observed at an optical microscope level (up to 1000 magnification) is schematically shown in the left (Figs. 6A and 7A).

5 The structure of fibers as observed at a scanning electron microscope (SEM) level (up to thirty thousand magnification) is schematically shown in the middle (Figs. 6B and 7B). The structure of fibers as observed at a transmission electron microscope (TEM)
10 level (up to one million magnification) is schematically shown in the right (Figs. 6C and 7C).

As shown in Figs. 6A to 6C, a graphen comprising a cylindrical shape along an elongated (longitudinal) direction (fiber axial direction) is
15 called a carbon nanotube (multi-wall nanotube if the cylindrical shape is a multi-structure). If the tube end is open, the electron emission threshold value is lowest. In other words, the carbon nanotubes are fibrous substance comprising graphens disposed
20 substantially parallel to the fiber axis.

Fibers comprising carbon formed at a relatively low temperature as the main composition are shown in Figs. 7A to 7C. The fibers are made of a lamination of graphens (from this reason, the fibers are also
25 called "graphite nanofibers"). More specifically, graphite nanofibers are fibrous substance made of a lamination of graphens stacked along the longitudinal

direction (fiber axial direction). In other words,
as shown in Figs. 7A to 7C, the graphite nanofibers
are fibrous substance made of a lamination of
graphens whose plane is not parallel to the fiber
5 axis.

Both the carbon nanotubes and graphite
nanofibers have the electron emission threshold of
about 1 V/ μ m or higher and about 10 V/ μ m or lower,
and are suitable for the material of an emitter (an
10 electron-emitting member) of an electron-emitting
device of the invention.

An electron-emitting device comprising graphite
nanofibers can emit electrons at a low intensity of
the electric field, can provide a large emission
15 current, can be manufactured easily, and provides
stable and good electron emission characteristics.
Comparing to the electron-emitting device comprising
a plurality of carbon nanotubes, the electron-
emitting device comprising a plurality of graphite
20 nanofibers can be expected to obtain more electron
emission current and/or stable electron emission.
For example, an electron-emitting device can be
formed by an emitter comprising of graphite
nanofibers (or carbon nanotubes) and electrodes for
25 controlling electron emission from the emitter. A
light-emitting apparatus such as a lamp can be formed
by using a light-emitting member which emits light

upon irradiation of electrons emitted from graphite nanofibers (or carbon nanotubes).

An image forming apparatus such as a display can be formed by disposing a plurality of electron-emitting devices using graphite nanofibers (or carbon nanotubes) and providing an anode electrode comprising a light-emitting member such as a phosphor and a drive circuit for controlling a voltage to be applied to each electron-emitting device. An electron source, a light-emitting apparatus and an image forming apparatus using electron-emitting devices comprising graphite nanofibers (or carbon nanotubes) can stably and reliably emit electrons without maintaining the inside at a ultra high vacuum, and can be manufactured very easily and with high reliability because they emit electrons at a low intensity of the electric field.

Fibers comprising carbon as the main composition to be used by the invention may be manufactured by any one of manufacture methods. One of such fiber manufacturing methods comprises a first step of preparing a catalyst substance (substance for promoting deposition of carbon) and a second step of decompose carbon containing gas by using the catalyst substance. Whether carbon nanotubes are formed or graphite nanofibers are formed depends upon the kind of catalyst and a decomposition temperature.

For example, the carbon containing gas may be:
hydrocarbon gas such as ethylene gas, methane gas,
propane gas, propylene gas and mixture gas of these
gases; CO gas; CO₂ gas; or vapor of organic solvent
5 such as ethanol and acetone.

The catalyst substance may be: metal selected
from a group consisting of Fe, Co, Pd and Ni; organic
or inorganic substance having such metal as the main
composition; or alloy made of at least two of the
10 above-described metals, these substances functioning
as nuclei for forming fibers.

If a substance which contains Pd and/or Ni is
used, it is possible to form graphite nanofibers at a
relatively low temperature (at least as low as 400°C).
15 If a substance which contains Fe and/or Co is used, a
temperature at which carbon nanotubes are formed is
required to be 800°C or higher. Since graphite
nanofibers can be formed at a relatively low
temperature if the substance which contains Pd and/or
20 Ni is used, it is preferable in that other components
are less adversely affected, power consumption can be
suppressed, and manufacture cost is low.

By using the characteristics that oxide of Pd
is reduced by hydrogen at a low temperature (room
25 temperature), it becomes possible to use palladium
oxide as the nuclei forming substance.

If palladium oxide is subjected to a hydrogen

reduction process, an initial aggregation of nuclei can be formed at a relatively low temperature (200°C or lower) without using thermal aggregation of metal thin films or formation and vapor deposition of ultra fine particles which has been used conventionally as a general nuclei forming technique.

An example of a method of manufacturing an electron-emitting device of this invention will be described with reference to the accompanying drawings.

Fig. 1 is a schematic diagram showing an example of a manufacture system used by the invention. Fig. 2 is a schematic cross sectional view of electrodes 11 and 12 formed on a substrate 10. Fig. 3 is a schematic cross sectional view showing an example of an electron-emitting device of the invention. Figs. 4A and 4B are a schematic plan view and a schematic cross sectional view showing an example of an electron-emitting device of the invention.

According to the invention, fibers comprising carbon as the main composition prepared separately are disposed in a first chamber 1, and a substrate 7 with electrodes is disposed in a second chamber 5. Fibers comprising carbon as the main composition are intended to be fixed to the substrate. The first and second chambers communicate with each other via a transport tube 4. The pressure in the first chamber

1 is set higher than that in the second chamber 5. This pressure difference transports aerosolized fibers comprising carbon as the main composition into the second chamber via the transport tube 4, and the
5 aerosolized fibers comprising carbon as the main composition are ejected at high speed from a nozzle 6 mounted at the end of the transport pipe 4 toward the substrate. Heat energy is generated when the aerosolized fibers with the substrate 7 (or the
10 electrodes on the substrate) at high speed. This heat energy fixes the fibers to the substrate 7 without using adhesive. Reference numeral 3 in Fig. 1 represents a ultra fine particle material (fibers comprising carbon as the main composition).

15 As an example of a fixing method, an aerosol type gas deposition method may be used. With the aerosol type gas deposition method used by the invention, fibers prepared separately and comprising carbon as the main composition in an aerosolizing
20 chamber (first chamber) 1 are aerosolized by aerosolizing gas introduced from an aerosolizing gas cylinder 2 into the aerosolizing chamber. The aerosolized fibers comprising carbon as the main composition are transported from the aerosolizing
25 chamber 1 into the film forming chamber (second chamber) 5 by using a difference between the pressure in the aerosolizing chamber 1 and that in the film

forming chamber 5. The aerosolized fibers comprising carbon as the main composition as well as the aerosolizing gas is ejected from the nozzle 6 mounted at the end of the transport pipe 4 positioned in the film forming chamber 5 toward the substrate 7 to fix (bond) the fibers to the substrate 7.

The gas (transport gas) for aerosolizing fibers comprising carbon as the main composition may by inert gas such as nitrogen gas, helium gas or mixture gas thereof. Non-oxidizing gas is particularly suitable. With such gas, fibers comprising carbon as the main composition such as carbon nanotubes or graphite nanofibers whose size is in the order of submicron are aerosolized in the upper space of the aerosolizing chamber. The aerosolized fibers are sucked into a sucking port located at the top of the aerosolizing chamber and transported via the transport pipe 4 into the film forming chamber (second chamber) to which a vacuum exhaust pump is coupled. The fibers are ejected from the nozzle 6 mounted at the end of the transport pipe 4, collide with the substrate 7 placed on a stage 8, and fixed (bonded) thereto.

In this invention, the substrate 7 is fixed to the stage 8 in the second chamber 5, and the stage 8 is moved so that fibers comprising carbon as the main composition of a desired quantity can be fixed to the

substrate in a desired area. By changing the motion speed of the stage 8, the density of fibers comprising carbon as the main composition to be fixed can be changed. The nozzle 6 is also movable. By
5 finely adjusting the relative positions of the nozzle 6 and stage 8, it is possible to finely and reliably fix (bond) fibers comprising carbon as the main composition to the substrate.

In this invention, it is preferable that during
10 a film forming process, the inside of the film forming chamber (second chamber) 5 is evacuated by the vacuum exhaust pump 9 and maintained to be a reduced pressure state (vacuum state lower than 760 Torr). This is because the mean free path of
15 aerosolized fibers comprising carbon as the main composition ejected from the nozzle 6 in the reduced pressure state becomes longer by about a three-digit as compared to the case wherein fibers are ejected at a normal pressure (atmospheric pressure), and the
20 fibers are hard to be affected by the scattering effects.

More specifically, aerosolized fibers comprising carbon as the main composition ejected in the air are scattered and the kinetic energy is lost.
25 It is therefore difficult or almost impossible to bond the fibers to a substrate. However, aerosolized fibers comprising carbon as the main composition

ejected from the nozzle 6 in the film forming chamber (second chamber) 5 in the reduced pressure state can be collided with the substrate (or the electrodes on the substrate) with a larger kinetic energy. This
5 kinetic energy is converted into heat energy which contributes to bond the fibers (each end in the longitudinal direction of each fiber) to the substrate, this fixation being the object of the invention.

10 Not all the fibers comprising carbon as the main composition transported are fixed (bonded) to the substrate (or electrode), but there is a high probability that the fibers ejected with their longitudinal direction ("fiber axial direction" shown
15 in Figs. 6A to 6C and 7A to 7C) directed to the vertical direction to the substrate plane and electrode planes above the substrate are tightly fixed (bonded) to the substrate and electrodes. This may be ascribed to that when the fibers ejected from
20 the nozzle 6 are fixed (bonded) to the substrate (or the electrodes) with the heat energy converted from the kinetic energy of the fibers and generated upon collision of the fibers on the substrate (or the electrodes), the smaller the collision area, the more
25 the heat energy is concentrated upon the collision area so that the fibers are likely to be fixed (attached). At the moment that the fiber collides

with the substrate (or the electrode), the collision area of the fiber (preferably, as described above, an end (end portion) in the longitudinal direction of the fiber) seems to be melted.

5 It is preferable that fibers comprising carbon as the main composition are straight and cylindrical carbon fibers not curved such as shown in Figs. 6A to 6C because carbon fibers standing substantially upright on the surface of the substrate 7 and the
10 electrode surfaces above the substrate can be fixed to the substrate and electrodes. Also in this invention, if fibers collide to the substrate (or the electrodes) along a direction different from the "fiber axial direction", the collision area increases
15 greatly so that the fibers are difficult to be fixed (attached) to the substrate (or the electrodes). It is therefore preferable that in order to stably fix fibers to the substrate (or the electrodes), the fiber diameter is several nm to several hundreds nm
20 (more preferably several nm or larger and 100 nm or smaller) and the length thereof is ten times or more and one hundred times or less of the diameter. In this invention, it is therefore preferable to use carbon nanotubes having a relatively high linearity
25 as the fibers comprising carbon as the main composition. From the above-described reasons, according to the manufacture method of the invention,

carbon fibers fixed to the substrate and electrodes have essentially the "fiber axial direction" substantially perpendicular to the substrate surface and electrode surfaces. According to the invention, 5 it is therefore easy to fix carbon fibers substantially vertically to the substrate surface and electrode surfaces. Accordingly, if an electron-emitting member is made of a number of carbon fibers disposed on a substrate by the manufacture method of 10 the invention, an electric field having a high intensity can be applied to the end of each fiber so that electron emission at a lower voltage is possible.

In this invention, it is preferable that colliding aerosolized fibers comprising carbon as the 15 main composition to the substrate (or the electrodes) is performed while the substrate is heated. This heating can improve tight contactness between the fibers comprising carbon as the main composition and the substrate (or the electrodes).

20 By moving the stage which holds the substrate while aerosolized fibers comprising carbon as the main composition are ejected from the nozzle, it is possible to continuously fix the fibers comprising carbon as the main composition to the substrate. If 25 masking using a metal mask or a resist mask is performed, fibers comprising carbon as the main composition can be fixed to the substrate only in a

desired area.

Aerosol of fibers comprising carbon as the main composition (gas dispersed with fibers comprising carbon as the main composition) is ejected from the nozzle 6 toward the substrate 7 preferably at a flow rate of 0.1 l/min or more, preferably at a flow rate of 1 l/min or more. Fibers comprising carbon as the main composition are ejected from the nozzle 6 toward the substrate 7 preferably at a speed of 0.1 m/sec or more, more preferably at a speed of 1 m/sec or more, or most preferably at a speed of 10 m/sec or more. In order to realize such flow rate and/or speed, the pressures in the first chamber 1 and second chamber 5 are properly set. A distance between the nozzle 6 and substrate 7 is preferably 10 cm or shorter, or more preferably 1 cm or shorter.

The substrate 7, 10 may be a quartz glass substrate, a glass substrate with reduced impurity contents such as Na partially replaced with K or the like, a soda lime glass substrate, a laminated substrate of a silicon substrate or the like laminated with SiO₂ by sputtering or the like, a ceramic insulating substrate such as alumina, or the like.

The material of the device electrode 11, 12 formed on the substrate is a general conductive material selected from a group consisting of, for

example, carbon; metal such as Ni, Au, Mo, W, Pt, Ti, Al, Cu and Pd or alloy thereof; nitride of such metal (e.g., nitride of Ti); carbide of such metal; boride of such metal; transparent conductive material such as $\text{In}_2\text{O}_3 - \text{SnO}_2$; semiconductor material such as polysilicon; and the like.

Preferably, the material of the device electrode formed on the substrate is selected from electroconductive materials of which Young's modulus not greater than 15. Further, as material constituting the electrode, the electroconductive materials of which Young's modulus is not greater than 10 are more desirable. Concrete examples of the electroconductive material of such Young's modulus are metals such as Sn, In, Au, Ag, Cu and Al, electroconductive materials containing at least two selected from the metals, alloys of the metals, or material containing as a main ingredient one or ones selected from the metals. According to the manufacturing method of the present invention, since the electrode is formed from the electroconductive material of Young's modulus not greater than 15, when the fiber containing carbon mainly collides with the electrode under the above described condition, the fiber containing carbon mainly is readily fixed onto the electrode (e.g. cathode).

After the substrate 7, 10 is cleaned

sufficiently with detergent, pure water, organic solvent or the like, electrode material is deposited on the substrate by vapor deposition, printing, sputtering or the like. Thereafter, the electrode
5 material is worked by, for example, photolithography, to form electrodes having desired shapes.

The distance between device electrodes 11 and 12, the length of each device electrode, the shape of each device electrode and the like are properly
10 designed in accordance with the application field. The distance between the device electrodes is preferably several nm or longer and several hundreds μm or shorter, or more preferably in the range from 1 μm or longer to 100 μm or shorter depending upon the
15 voltage applied across the electrodes and the like. The device electrode length is in the range from several μm or longer to several hundreds μm or shorter depending upon the electrode resistance value, electron emission characteristics and the like. The
20 device electrode thickness is set in a range from several tens nm or longer to several tens μm or shorter.

The electron-emitting device manufactured by the manufacture method of the invention may take
25 various structures. For example, as shown in Fig. 5, as a preferred structure of the electron-emitting device, on the surface of a substrate 10, a drawing

electrode (called a "gate electrode" where appropriate) 11 and a cathode electrode 12 are disposed spaced from each other. Fibers 13 comprising carbon as the main composition are
5 disposed on the cathode electrode 12 by the manufacture method of the invention. Fig. 5 is a schematic diagram showing the outline structure of an evaluation system for measuring the electron emission characteristics of an electron-emitting device
10 manufactured by the manufacture method of the invention. In Fig. 5, reference numeral 9 represents a vacuum exhaust pump, reference numeral 14 represents a phosphor, reference numeral 15 represents a vacuum system, and reference numeral 20
15 represents an anode electrode for capturing an emission current I_e emitted from an electron-emitting portion (fibers comprising carbon as the main composition) of the device.

An electron-emitting device having a gap of
20 several μm between the drawing electrode and cathode electrode as well as the anode electrode 20 are installed in the vacuum system 15 shown in Fig. 5. The inside of the vacuum system 15 is sufficiently evacuated by the vacuum exhaust pump 9 to a pressure
25 of about 10^{-5} Pa. The distance H between the substrate and anode electrode 20 is several mm, for example, 2 mm or longer and 8 mm or shorter. As

shown in Fig. 5, a high voltage source applies a high voltage V_a of several kV, for example, 1 kV or higher and 10 kV or lower, to the anode electrode 20.

Upon application of a drive voltage (device
5 voltage) V_f of about several tens V and the anode voltage V_a , electrons are emitted and the electron emission current I_e is obtained. A device current is represented by I_f .

It is preferable for the electron-emitting
10 device that in order to suppress scattering on the gate electrode 11, the plane substantially in parallel to the substrate 10 surface including the surface of the fibers 13 is positioned more remotely from the substrate 10 surface than the plane
15 substantially in parallel to the substrate 10 surface including the partial surface of the gate electrode 11 (refer to Figs. 4A, 4B and 5). In other words, it is preferable for the electron-emitting device of the invention that the plane substantially in parallel to
20 the substrate 10 surface including the surface of the fibers 13 is positioned between the anode electrode 20 and the plane substantially in parallel to the substrate 10 surface including the partial surface of the lead electrode 11 (refer to Figs. 4A, 4B and 5).

25 It is also preferable for the electron-emitting device of the invention that in order to substantially eliminate scattering on the gate

electrode 11, the fibers 13 having carbon as the main composition are positioned at a height s (distance between the plane substantially in parallel to the substrate 10 surface including the surface of the fibers 13 and the plane substantially in parallel to the substrate 10 surface including the partial surface of the gate electrode 11).

The height s depends upon a ratio of the vertical electric field to the horizontal electric field ($\text{vertical electric field intensity} / \text{horizontal electric field intensity}$). The larger the ratio of the vertical electric field to the horizontal electric field, the height becomes greater. The higher the horizontal electric field intensity, the greater height is necessary. A practical range of the height s is from 10 nm or higher to 10 μm or lower.

The "horizontal electric field" used in the invention can be said as "electric field along a direction substantially in parallel to the substrate 10 surface" or "electric field along a direction along which the gate electrode 11 and cathode electrode 12 face each other". The "vertical electric field" used in the invention can be said as "electric field along a direction substantially vertical to the substrate 10 surface" or "electric field along a direction along which the substrate 10

and anode electrode 20 face each other".

In the electron-emitting device of the invention, the electric field (horizontal electric field) $E1 = Vf/d$ in a drive state is set to the
5 electric field between the anode electrode and cathode electrode (vertical electric field) $E2 = Va/H$ or larger and 50 times of $E2 = Va/H$ or smaller, where d is the distance between the cathode electrode 12 and gate electrode 11, Vf is a potential difference
10 between the cathode electrode 12 and gate electrode 11 while the electron-emitting device is driven, H is the distance between the anode electrode 20 and the substrate 10 on which the device is disposed, and Va is a potential difference between the anode electrode
15 20 and cathode electrode 12.

By setting the electric field in the above-described manner, the number of electrons emitted from the cathode electrode 12 side and bombarded on the gate electrode 11 can be reduced. The spread of
20 emitted electrons can therefore be narrowed and the electron-emitting device having a high efficiency can be obtained.

An example of the electron source manufactured by the method of the invention will be described
25 briefly.

As a layout of electron-emitting devices on a substrate, there are a ladder layout and a matrix

layout. In the latter, on m X-directional wirings, n Y-directional wirings are disposed with an interlayer insulating layer being interposed therebetween, and X- and Y-directional wirings are connected to a pair
5 of device electrodes (gate electrode and cathode electrode) of each electron-emitting device. X- and Y-directional wirings are made of conductive metal formed on an electron source substrate by vapor deposition, printing, sputtering or the like.
10 Voltage is applied via the wirings. The interlayer insulating layer is made of SiO_2 or the like deposited by vapor deposition, printing, sputtering or the like.

Device electrodes of the electron-emitting
15 devices are electrically connected by m X-directional wirings and n Y-directional wirings and interconnections made of conductive metal or the like deposited by vapor deposition, printing, sputtering or the like.

20 Next, as an example of the light-emitting apparatus manufactured by the method of the invention, the light-emitting apparatus using an electron source of the matrix layout will be described briefly.

The light-emitting apparatus is mainly
25 constituted of an electron source substrate disposed with electron-emitting devices, a face plate made of a glass substrate on the inner surface of which an

inner light-emitting member (phosphor film), a metal back and the like are formed, and a support frame.

The phosphor film is made of only phosphor for a monochromatic phosphor film. For a color phosphor
5 film, the phosphor film is made of phosphor and a black conductive member called a black stripe or black matrix depending upon the layout of phosphor members.

Phosphor is coated on the glass substrate by
10 precipitation or printing. The metal back is formed by depositing Al by vacuum deposition or the like after the inner surface of the phosphor film is subjected to a planarizing process (filming).

Next, an example of an image forming apparatus
15 manufactured by the method of the invention will be described briefly.

The image forming apparatus is mainly constituted of a light-emitting apparatus, a scan circuit, a control circuit, a shift register, a line
20 memory, a sync signal separation circuit, a modulating signal generator and a d.c. voltage source.

The invention will be described in more detail by using embodiments.

First Embodiment

25 Fig. 2 is a schematic cross sectional view showing a substrate with electrodes according to the embodiment. Fig. 3 is a schematic cross sectional

view of an electron-emitting device of the embodiment. In Figs. 2 and 3, reference numeral 10 represents an insulating substrate, reference numeral 11 represents a lead electrode (gate electrode), reference numeral 12 represents a cathode electrode, and reference numeral 13 represents fibers (emitter) having carbon as the main composition.

The manufacture processes for the electron-emitting device of the embodiment will be described.

First, a quartz glass substrate was prepared as a substrate, washed sufficiently with organic solvent, and then dried at 120°C. On the washed quartz substrate, Ti of 5 nm in thickness and polysilicon (doped with arsenic) of 30 nm in thickness were deposited in succession by sputtering.

Next, by using a resist film patterned by photolithography as a mask, the deposited polysilicon (doped with arsenic) layer and Ti layer were dry-etched by using CF_4 gas to form a gate electrode and a cathode electrode having an electrode gap of 5 μm .

Next, carbon nanotubes prepared in advance were disposed in an aerosolizing chamber, and the substrate with the electrodes formed as described above was disposed in the aerosolizing chamber. Next, helium gas was introduced into the aerosolizing chamber to aerosolize the carbon nanotubes. By utilizing a difference between the pressure (about

200 KPa) in the aerosolizing chamber and the pressure (about 60 Pa) in a film forming chamber, the aerosolized carbon nanotubes were introduced into the film forming chamber via a transport tube
5 communicating with the aerosolizing chamber and film forming chamber. The aerosolized carbon nanotubes were ejected from a nozzle mounted at the end of the transport tube positioned in the film forming chamber toward the area of the substrate to which the carbon
10 nanotubes are desired to be fixed. The carbon nanotubes used were formed by dissolving ethylene gas at a temperature of 800°C by using Co as catalyst substance.

The substrate to which the aerosolized carbon
15 nanotubes were ejected was observed with a scanning electron microscope. It was confirmed that the carbon nanotubes were fixed generally vertically to the substrate surface (electrode surface).

The electron emission characteristics of the
20 device manufactured in the above manner were measured as in the following. The device was placed in a vacuum system such as shown in Fig. 5, the inside of the vacuum system was evacuated with a vacuum exhaust pump to a pressure of 2×10^{-5} Pa, and an anode
25 voltage $V_a = 10$ kV was applied to the anode electrode spaced apart by $H = 2$ mm from the device as shown in Fig. 5. The device current I_f and electron emission

current I_e of the device applied with a drive voltage were measured. It was confirmed that the stable and excellent electron emission characteristics were maintained for a long period.

5 Second Embodiment

In the manner similar to the first embodiment, a drawing electrode 11 and a cathode electrode 12 were formed on a substrate. In the second embodiment, as shown in Figs. 4A and 4B, the thickness of the cathode electrode 12 was made thicker than that of the drawing electrode 11. Fig. 4A is a schematic plan view of the electron-emitting device of this embodiment, and Fig. 4B is a schematic cross sectional view taken along line 4B-4B in Fig. 4A.

15 Next, Cr was deposited on the whole surface of the substrate to a thickness of about 100 nm by EB deposition.

A resist pattern of positive photoresist was formed by photolithography. Next, by using the patterned photoresist as a mask, Cr exposed in an opening of the mask was removed by cerium nitride based etchant to thereby expose a partial surface area (100 μm square) of the cathode electrode to be covered with electron-emitting members (fibers comprising carbon as the main composition).

25 After the resist mask was removed, carbon nanotubes are fixed to the substrate in the manner

similar to the first embodiment. In this case, the carbon nanotubes were fixed while the substrate was heated to 200°C. The electron emission characteristics of the electron-emitting device of this embodiment were measured in the manner similar to the first embodiment. It was confirmed that the stable and excellent electron emission characteristics were maintained for a long period.

Third Embodiment

10 In the manner similar to the first embodiment, a drawing electrode and a cathode electrode were formed on a substrate. Next, a metal mask having an opening in the area where electron-emitting members are to be formed was fixed to the substrate.

15 Next, fibers comprising carbon as the main composition were fixed to the opening area on the substrate in the manner similar to the first embodiment, excepting that the pressure of an aerosolizing chamber was set to about 70 KPa, the pressure of a film forming chamber was set to about 200 Pa and graphite nanofibers were used instead of carbon nanotubes. In this case, fibers were fixed while the substrate was heated to 200°C. The nozzle used for film formation had a slit shape and the substrate was scanned so that the nozzle scanned over the opening.

The electron emission characteristics of the

electron-emitting device of this embodiment were measured in the manner similar to the first embodiment. It was confirmed that the stable and excellent electron emission characteristics were
5 maintained for a long period.

As described so far, according to the manufacture method of the invention, it is possible to directly fix fibers comprising carbon as the main composition such as carbon nanotubes and graphite
10 nanofibers to a substrate and to greatly shorten and simplify the processes necessary for electron-emitting device manufacture. Further, since the electron-emitting device manufacture method of the invention can fix carbon nanotubes vertically to the
15 substrate surface, an electric field of a higher intensity can be concentrated upon each fiber having carbon as the main composition. Therefore, an electron-emitting device having excellent electron emission characteristics can be manufactured and also
20 an electron source, a light-emitting apparatus and an image forming apparatus using such electron-emitting devices can be manufactured.

WHAT IS CLAIMED IS:

1. A method of manufacturing an electron-emitting device wherein:

5 a material comprising carbon as the main composition is aerosolized and transported together with gas, and tightly attached to a substrate via a nozzle.

2. A method according to claim 1, wherein the
10 material comprising carbon as the main composition is fibers comprising carbon as the main composition.

3. A method according to claim 2, wherein the
15 fibers comprising carbon as the main composition are at least ones selected from a group consisting of graphite nanofibers, carbon nanotubes, amorphous carbon fibers and carbon nanohorns.

4. A method of manufacturing an electron-emitting device, the method comprising:
20

(A) a step of preparing fibers comprising carbon as main composition in a first chamber;

(B) a step of disposing a substrate in a second chamber; and

25 (C) a step of colliding the fibers comprising carbon as the main composition with the substrate via a transport tube communicating with the first and

second chamber by setting a pressure in the first chamber higher than a pressure in the second chamber, to fix the fibers comprising carbon as the main composition to the substrate.

5

5. A method of manufacturing an electron-emitting device, the method comprising:

(A) a step of preparing fibers comprising carbon as main composition in a first chamber;

10 (B) a step of disposing a substrate formed with a cathode electrode on a surface thereof in a second chamber; and

(C) a step of colliding the fibers comprising carbon as the main composition with the cathode
15 electrode via a transport tube communicating with the first and second chamber by setting a pressure in the first chamber higher than a pressure in the second chamber, to fix the fibers comprising carbon as the main composition to the cathode electrode.

20

6. A method according to claim 4 or 5, wherein the fibers comprising carbon as the main composition are dispersed in gas in the first chamber.

25 7. A method according to claim 6, wherein the gas is non-oxidizing gas.

8. A method according to claim 4 or 5, wherein the inside of the second chamber is in a reduced pressure state.

5 9. A method according to claim 4 or 5, wherein the fibers comprising carbon as the main composition are aerosolized in the first chamber.

10 10. A method according to any one of claims 1 to 5, wherein the fibers comprising carbon as the main composition are fixed to the substrate by heat energy generated when the fibers comprising carbon as the main composition collide with the substrate.

15 11. A method according to claim 4 or 5, wherein the fibers comprising carbon as the main composition are at least ones selected from a group consisting of graphite nanofibers, carbon nanotubes, amorphous carbon fibers and carbon nanohorns.

20

12. A method according to claim 4, wherein a first conductive layer is disposed on the substrate and the fibers comprising carbon as the main composition are fixed to the substrate through the
25 first conductive layer.

13. A method according to claim 12, wherein a

second conductive layer is disposed on the substrate, the second conductive layer being spaced apart from the first conductive layer.

5 14. A method of manufacturing an electron source having a plurality of electron-emitting devices wherein the electron-emitting device is manufactured by the method as recited in any one of claims 1 to 5.

10

 15. A method of manufacturing an image forming apparatus having an electron source and a light emitting member wherein the electron source is manufactured by the method as recited by claim 14.

15

 16. A method of manufacturing a light-emitting apparatus having electron-emitting devices and light-emitting members wherein the electron-emitting device is manufactured by the method as recited in any one
20 of claims 1 to 5.

 17. An electron-emitting device comprises:

 (A) an electrode; and

 (B) carbon fiber having two ends in an axial
25 direction of the carbon fiber,

 wherein one of the ends is melted and is directly bonded to the electrode.

18. A method of manufacturing a substrate having a number of fibers comprising carbon as main composition, comprising:

(A) a step of preparing fibers comprising
5 carbon as main composition in a first chamber;

(B) a step of disposing a substrate in a second chamber; and

(C) a step of colliding the fibers comprising carbon as the main composition with the substrate via
10 a transport tube communicating with the first and second chamber by setting a pressure in the first chamber higher than a pressure in the second chamber, to fix the fibers comprising carbon as the main composition to the substrate.

15

19. An electron-emitting device comprising:

(A) a substrate with an electrode; and

(B) carbon fiber having two ends in a longitudinal direction of the carbon fiber,
20 wherein one of the ends is melted and is directly bonded to the substrate.

20. A method according to claim 12,
wherein

25 said first conductive layer is formed from a material of which Young's modulus is not greater than 15.

21. A method according to claim 12,
wherein

said first electroconductive layer is formed
from metal selected from Sn, In, Au, Ag, Cu and Al,
5 electroconductive material containing at least two
metals selected from Sn, In, Au, Ag, Cu and Al, or an
electroconductive material containing as a main
ingredient metal selected from Sn In, Au, Ag, Cu and
Al.

10

ABSTRACT OF THE DISCLOSURE

A method of manufacturing an electron-emitting device having excellent electron emission characteristics is provided in which fibers
5 comprising carbon as the main composition are fixed (bonded) to a substrate in a desired area and at a desired density with simple processes and inexpensive manufacture cost, and a manufacture method for an electron source, a light-emitting apparatus and an
10 image forming apparatus using such electron-emitting devices is provided. A method of manufacturing an electron-emitting device made of material comprising carbon as main composition by an aerosol type gas deposition method in which the material comprising
15 carbon as the main composition is aerosolized and transported together with gas, and tightly attached (bonded) to a substrate via a nozzle.

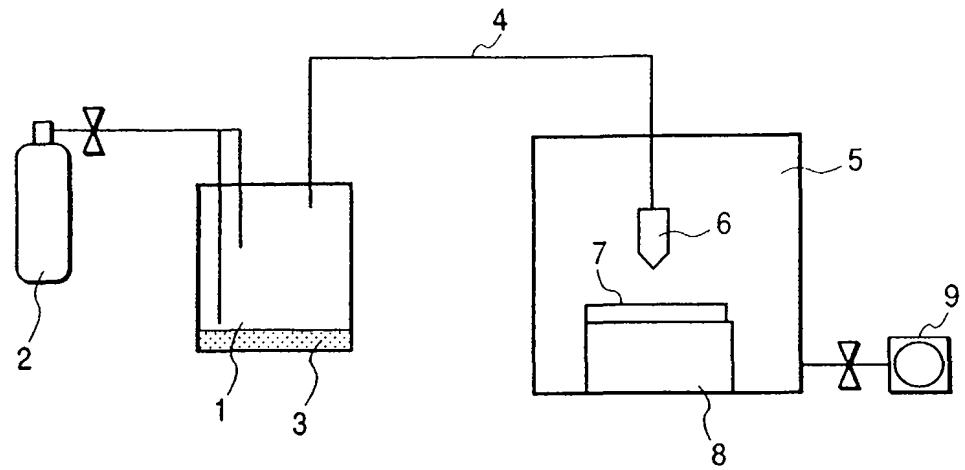
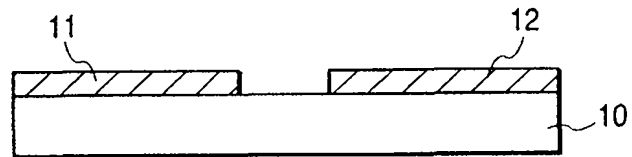
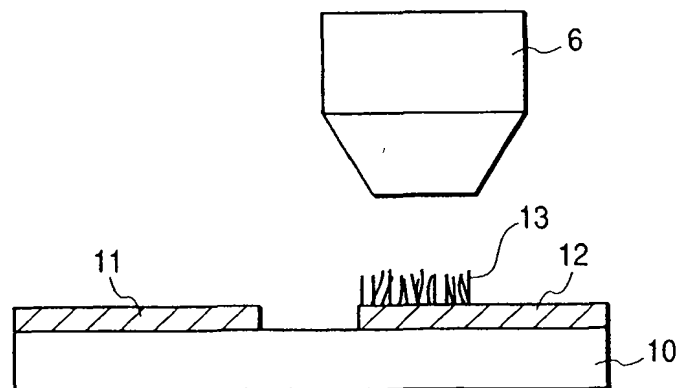
FIG. 1**FIG. 2****FIG. 3**

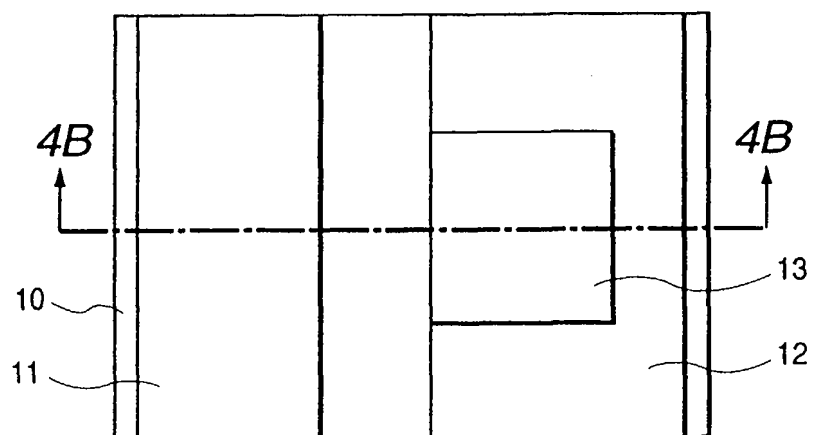
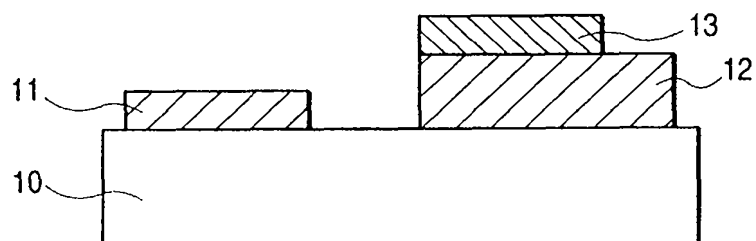
FIG. 4A*FIG. 4B*

FIG. 5

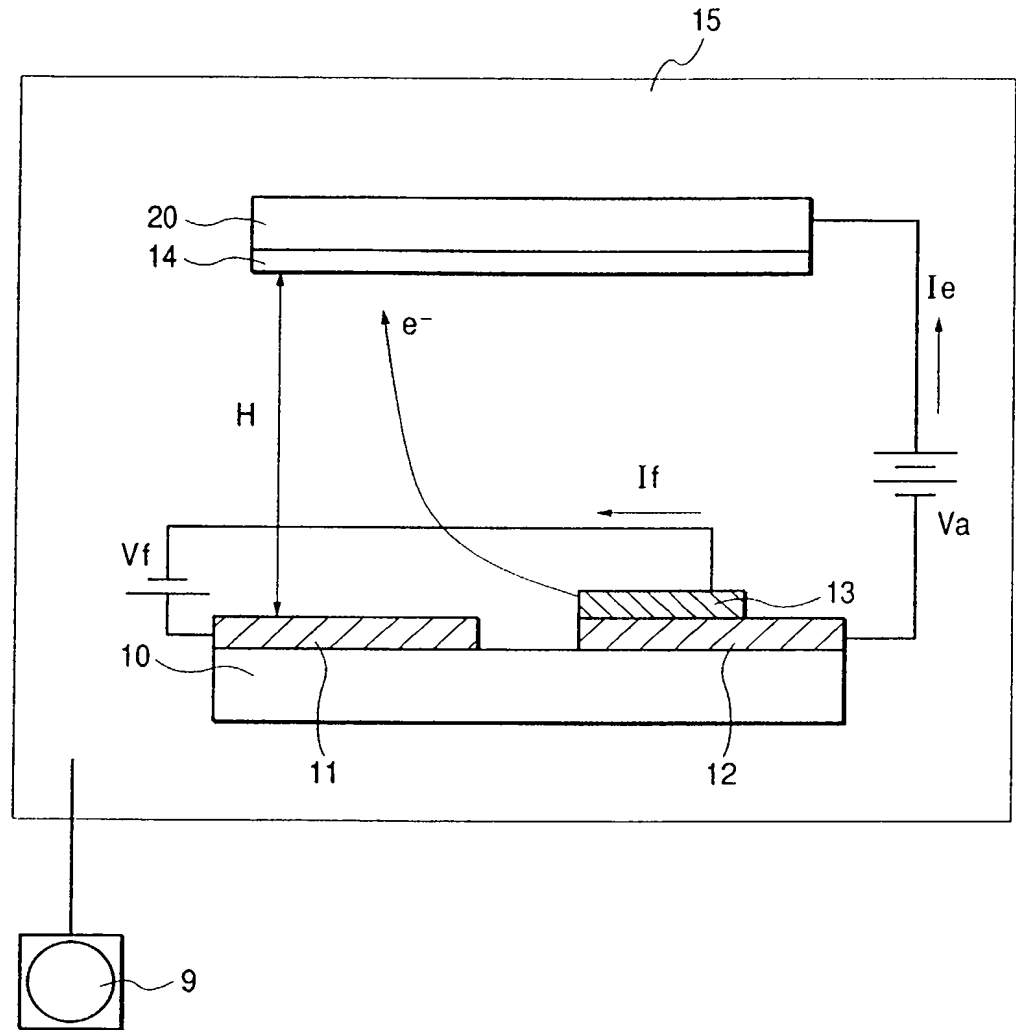


FIG. 6A

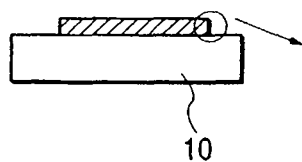


FIG. 6B

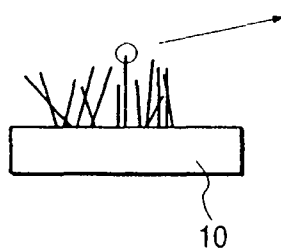


FIG. 6C

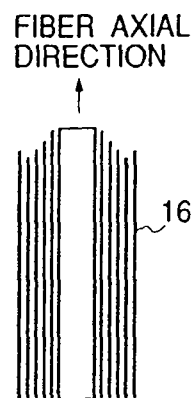


FIG. 7A

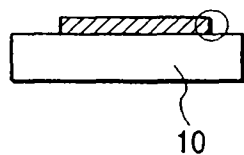


FIG. 7B

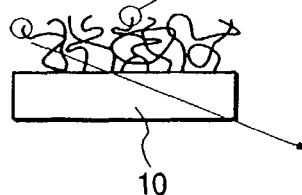
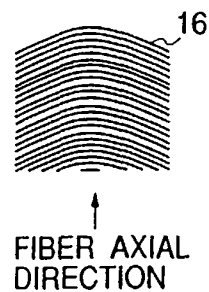
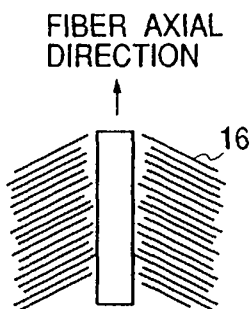


FIG. 7C



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ELECTRON-EMITTING DEVICE, ELECTRON SOURCE, IMAGE
FORMING APPARATUS, AND METHOD OF MANUFACTURING
ELECTRON-EMITTING DEVICE AND ELECTRON SOURCE

5 BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an
electron-emitting device, an electron source using
the same, and an image forming apparatus serving as a
10 television broadcasting display apparatus, a display
apparatus for a video conference system or computer,
or an optical printer using a photosensitive drum or
the like.

Related Background Art

15 An FE (Field Emission) electron-emitting device
which emits electrons from a metal surface by
applying a high field of 10^6 V/cm or more to a metal
has received a great deal of attention as one of cold
electron sources.

20 In recent years, flat display apparatuses using
liquid crystals have been replacing CRTs in image
forming apparatuses such as a display apparatus. The
flat display apparatuses are not of self-emission
type and require a backlight, and thus demands arise
25 for self-emission display apparatuses.

If an FE cold electron source becomes

The attached application:

U.S. Application No.: 10/235,809

Filing Date: 9/6/02

Group Art Unit: 2878

is part of an IDS filed in U.S. Application No.: 09/94,595

commercially available, it implements a flat self-emission image display apparatus, contributing to low power consumption and light weight.

A known example of a vertical FE electron
5 source is one disclosed in C.A. Spindt, "Physical Properties of Thin-Film Field Emission Cathodes with Molybdenum Cones", J. Appl. Phys., 47, 5248 (1976).

A diode structure in which a carbon nanotube is formed close to one terminal of an electrode is
10 described in SID (Society for Information Display) Digest p. 386, 2000. By shifting the electron-emitting member to one terminal of the electrode, a higher field is formed at the terminal than at the center of the electrode. The high-field
15 region formed only at the end of the electron-emitting region narrows the orbit of emitted electrons, obtaining a small electron beam spot.

Also, an electron-emitting device with a triode structure (only section) is proposed in 17th IDW
20 (International Display Workshop) Digest p. 1005, 2000. This structure is shown in Fig. 7. In Fig. 7, an electron-emitting member is formed from a substrate 71, lower electrode (gate electrode) 72, insulating layer 73, upper electrode (cathode) 74, and carbon
25 nanotubes 75. An anode (fluorescent substance) 76 is arranged above the electron-emitting member. The

insulating layer 73 is formed from two, SiO₂ and polyimide insulating layers. In this device, the lower electrode 72 is set to a high potential to form a high field between the upper and lower electrodes.

5 The field causes the carbon nanotubes 75 formed on the upper electrode 74 to emit electrons, which reach the anode 76 serving as a fluorescent substance.

SUMMARY OF THE INVENTION

10 It is reported that a conventional carbon nanotube exhibits a threshold field of several V/ μ m necessary for electron emission. The use of an electron-emitting material having a low threshold field for an electron-emitting device with the triode
15 structure decreases the voltage necessary for electron emission. This reduces not only the cost of the driving apparatus but also the power consumption.

However, when a high voltage is applied between the anode and the cathode, electrons may be directly
20 emitted by the electron-emitting member on the cathode and reach the anode depending on conditions owing to a field formed between the cathode and the anode without applying any voltage to the gate electrode. In this situation, the orbit of electrons
25 is different from that of electrons emitted by applying a voltage to the gate. Electrons do not

reach a prospective region on the anode, and modulation by the gate electrode cannot be achieved. This causes misregistration in the image forming apparatus as an abnormal lights-on error, degrading
5 the image quality. This phenomenon at even one portion in the image forming apparatus leads to an apparatus defect to narrow the design width of the image forming apparatus.

It is an object of the present invention to
10 solve the above-described problems.

According to the present invention, there is provided an electron-emitting device comprising: an electron-emitting member containing carbon as a main component; and an extraction electrode arranged near
15 the electron-emitting member, wherein an electron-emitting threshold field (a threshold electric field needed to starting of electron emission) of the electron-emitting member is low at a portion close to the extraction electrode and high at
20 a portion apart from the extraction electrode.

According to the present invention, there is provided a method of manufacturing an electron-emitting device having an electron-emitting member containing carbon as a main component, and an
25 extraction electrode arranged near the electron-emitting member, the method comprising a threshold field control step of performing processing

so as to give an electron-emitting threshold field of the electron-emitting member a different value depending on a distance from the extraction electrode.

- 5 In the above-described electron-emitting device, an example of the electron-emitting member containing carbon as a main component includes a plurality of fibrous carbon elements, and the fibrous carbon elements are made of a material which has an
- 10 sp^2 bond and is selected from the group consisting of a graphite nanofiber, a carbon nanotube, amorphous carbon, and a mixture of at least two materials selected from the group consisting of the graphite nanofiber, the carbon nanotube, and amorphous carbon.
- 15 Another example of the electron-emitting member containing carbon as a main component includes a thin film made of a material that has an sp^3 bond and is selected from the group consisting of diamond, diamond-like carbon, amorphous carbon, and a mixture
- 20 of at least two materials selected from the group consisting of diamond, diamond-like carbon, and amorphous carbon.

- In the above-described manufacturing method, an example of the threshold field control step includes
- 25 the step of partially etching the electron-emitting member in an atmosphere of a substance which can chemically react with the electron-emitting member.

An example of the substance which can chemically react with the electron-emitting member includes water, oxygen, and carbon dioxide. In the threshold field control step, the electron-emitting
5 member can emit electrons. At this time, a negative potential with respect to the electron-emitting member is applied to the extraction electrode, and a positive potential with respect to the electron-emitting member is applied to an anode
10 arranged in opposite to the electron-emitting member via vacuum.

There is provided an electron source comprising at least one electron-emitting device array constituted by arranging a plurality of
15 electron-emitting devices described above parallel to each other and connecting the electron-emitting devices. There is provided an electron source comprising at least one electron-emitting device array constituted by arranging a plurality of
20 electron-emitting devices described above, wherein low-potential supply wiring lines and high-potential supply wiring lines which drive the electron-emitting devices are arranged in a matrix. There is provided an image forming apparatus comprising the
25 above-described electron source, and an image forming member which forms an image by electrons emitted by the electron source, wherein an electron-emitting

amount of each electron-emitting device of the electron source is controlled by an information signal.

In a method of manufacturing an electron source
5 in which at least one array of a plurality of electron-emitting devices is arranged on an insulating substrate, and low-potential supply wiring lines and high-potential supply wiring lines which drive the electron-emitting devices are arranged in a
10 matrix, the electron-emitting devices are manufactured by the above-described manufacturing method. An example of the threshold field control step is line-sequentially performed by selecting an array of the electron-emitting devices and driving
15 each array. Another example of the threshold field control step is point-sequentially performed by selecting an electron-emitting device and driving the selected device.

The electron-emitting device and electron
20 source according to the present invention can emit electrons from substantially only a region of the electron-emitting member close to the extraction electrode. The image forming apparatus constituted using the electron source can form a high-quality
25 image almost free from brightness nonuniformity and abnormal lights-on errors.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A and 1B are views showing an example of a basic electron-emitting device according to the present invention;

5 Fig. 2 is a view for explaining the threshold field control step in the electron-emitting device manufacturing method of the present invention;

 Fig. 3 is a view showing an arrangement when the electron-emitting device according to the present
10 invention is operated;

 Figs. 4A, 4B, 4C, 4D, 4E, and 4F are views showing steps in manufacturing an electron-emitting device according to Example 1;

 Fig. 5 is a view showing an electron-emitting
15 device according to Example 2;

 Fig. 6 is a view showing an arrangement of a matrix circuit using a plurality of electron-emitting devices according to the present invention;

 Fig. 7 is a view showing a conventional
20 multilayered FE device;

 Fig. 8 is a view showing a form of fibrous carbon; and

 Fig. 9 is a view showing another form of fibrous carbon.

25

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

A preferred embodiment of the present invention

will be described below, but the present invention is not limited by the embodiment.

One method of forming electron-emitting members having different electron-emitting threshold field
5 depending on the distance from an extraction electrode in the present invention will be explained with reference to Fig. 2.

In Fig. 2, an extraction electrode (also referred to as a "gate electrode" or "gate") 2, a
10 cathode electrode (also referred to as an "emitter electrode") 3, an electron-emitting member 4, and a conductive material 5 are formed on a rear substrate 1. This electron-emitting device is set in a vacuum vessel 20. An anode electrode 22 is formed on an
15 anode substrate 21. Equipotential lines 23 are formed between the anode and the electron-emitting device, and represent given potentials. An uppermost plane 24 of the electron-emitting member is defined by a height s from the gate electrode. The vacuum
20 vessel 20 is connected to an evacuation apparatus 25, and a vessel 26 contains a substance which reacts chemically or physically with the electron-emitting member. Both the cathode electrode 3 and conductive material 5 may be called a cathode electrode (also
25 referred to as an "emitter electrode").

A gap between the electrodes 2 and 3 is defined as a distance d . A distance between the rear

substrate 1 and the anode substrate 21 is defined as a distance H.

First, the device is arranged in the vacuum vessel 20, and a vacuum is produced using the evacuation apparatus 25. A voltage is applied to the device so as to set the extraction electrode 2 to a low potential and the electron-emitting member 4 to a high potential. Then, a higher potential V_a than that of the electron-emitting member 4 is applied to the anode 22 which faces the substrate 1 by the distance H. At this time, the equipotential lines 23 as shown in Fig. 2 are formed.

As is apparent from Fig. 2, an equipotential line 23 having a specific potential is formed on the surface of the electron-emitting member 4 such that the equipotential line 23 is spaced apart from the electron-emitting member 4 in a region closest to the gate electrode 2 and comes close to the electron-emitting member 4 as the line 23 is spaced apart from the gate electrode 2. That is, on the surface of the electron-emitting member 4, the electric field intensity is low in a region close to the gate electrode 2 and high in a region apart from the gate electrode 2.

In this state, an electric field intensity in a region apart from the gate electrode reaches a electric field strength(intesity) enough to emit

electrons under proper conditions of the anode voltage V_a and height H . Electrons are emitted from an electron-emitting member in a region apart from the gate electrode, whereas no electrons are emitted
5 in a region close to the gate electrode.

In this situation, the valve (not shown) of the vessel 26 containing a substance which reacts with the electron-emitting member 4 is opened to introduce a small amount of reactive substance into the vacuum
10 vessel 20.

The substance which reacts with the electron-emitting member 4 mainly includes two types of substances: a substance which reacts chemically and a substance which reacts physically. Examples of
15 the substance which reacts chemically are O_2 , H_2O , and CO_2 for a carbon electron-emitting member 4. The substance which reacts physically is a substance which changes into a charged particle by an electron beam, and is preferably a substance with a relatively
20 large mass number such as Ar. The introduction pressure of the substance gas, which changes depending on the type of gas, is generally about 1×10^{-4} Pa to 1×10^1 Pa in order to chemically react with the electron-emitting member 4 during the
25 electron emission, and about 1×10^{-6} Pa to 1×10^1 Pa in order to physically react.

In this situation, the portion which emits

electrons is highly chemically active due to high temperatures or the like. At this portion, chemical reaction with the electron-emitting member progresses at a higher speed than in a region where no electrons
5 are emitted. The electron-emitting member is chemically etched away, and changes its form or disappears, thus increasing the electron-emitting threshold field.

At the portion which emits electrons, emitted
10 electrons ionize the gas of the substance which is introduced into vacuum and physically reacts. Ions collide against the electron-emitting portion. Then, the electron-emitting portion is etched away, and changes its form or disappears, increasing the
15 electron-emitting threshold field.

In the threshold field control step accompanied with potential application according to the present invention, a portion which easily emits electrons (easily enhances the electric field intensity)
20 intensively reacts and is etched in the electron-emitting region to remove a portion where the electric field is excessively concentrated. As a result, electron-emitting members having different electron-emitting threshold fields are formed in the
25 direction of distance from the gate.

In the present invention, a bundle of a plurality of fibrous carbon is preferably used as the

electron-emitting member 4. The fibrous carbon has a very large aspect ratio and easily enhances the electric field intensity. The fibrous carbon can therefore emit electrons at a low voltage, and is
5 preferably used as the electron-emitting member 4 of the present invention.

The "fibrous carbon" in the present invention can be called a "pillar substance containing carbon as a main component" or "linear substance containing
10 carbon as a main component" or "carbon fiber". The "fibrous carbon" can also be referred to as a "fiber containing carbon as a main component". More specifically, the "fibrous carbon" in the present invention includes a carbon nanotube, graphite
15 nanofiber, and amorphous carbon fiber. Of these materials, the graphite nanofiber is the most preferable as the electron-emitting member.

A material preferably adopted as the electron-emitting member 4 is a bundle of a plurality
20 of carbon fibers.

The fibrous carbon(carbon fiber) has a threshold field of several V/ μ m. Figs. 8 and 9 show forms of the fibrous carbon. In Figs. 8 and 9, a form observed at the optical microscope level (up to
25 X1,000) is schematically shown on the left side; a form observed at the scanning electron microscope (SEM) level (up to X30,000), at the center; and a

carbon form observed at the transmission electron microscope (TEM) level (up to X1,000,000), on the right side.

As shown in Fig. 8, the cylindrical form of
5 graphene (multiple cylindrical structure is called a multi-wall nanotube) is called a carbon nanotube, and its threshold field decreases the most in a structure in which the distal end of the tube is open. More specifically, the carbon nanotube is a fibrous
10 substance in which graphene is so arranged as to surround (cylindrically) the tube in the longitudinal direction (fiber axial direction). In other words, the carbon nanotube is a fibrous substance in which graphene is arranged substantially parallel to the
15 fiber axis.

Fig. 9 shows a fibrous carbon form which can be generated at relatively low temperatures. Fibrous carbon with this form is made from a graphene multilayered member (thus called a "graphite
20 nanofiber"). More specifically, the graphite nanofiber means a fibrous substance in which graphene is stacked in the longitudinal direction (fiber axial direction). In other words, the graphite nanofiber is a fibrous substance in which graphene is arranged
25 not parallel to the fiber axis.

One plane(sheet) of graphite is called a "graphen" or a "graphen sheet". More specifically,

graphite comprises a plurality of stacked or layered carbon planes. Each carbon plane comprises a repeated hexagon having a carbon atom at each vertex thereof and having a covalent bond along each side thereof. The covalent bond is caused by sp² hybrid orbitals of carbon atoms. Ideally, the distance(interval) between the neighboring carbon planes is 3.354×10^{-10} m. Each carbon plane is called "graphene" or a "graphene sheet".

10 Either fibrous carbon has an electron-emitting threshold field of about 1 to 10 V/ μ m, and is preferable as the material of the electron-emitting member 4 in the present invention.

 In particular, an electron-emitting device
15 using a graphite nanofiber aggregate can emit electrons with a low field, obtain a large emission current, be easily manufactured, and provide an electron-emitting device having a stable electron-emitting characteristic. Comparing to the
20 electron-emitting device comprising a plurality of carbon nanotubes (a bundle of carbon nanotubes), the electron-emitting device comprising a plurality of graphite nanofibers(a bundle of graphite nanofibers) can be expected to obtain more electron emission
25 current and/or stable electron emission.

 For example, an electron-emitting device can be formed by using the graphite nanofiber as an emitter

and preparing an electrode which controls electron emission from this emitter. A light-emitting apparatus such as a lamp can be formed by using a light-emitting member which emits light by
5 irradiation of electrons emitted by the graphite nanofiber. An image display apparatus such as a display can also be constituted by arraying a plurality of electron-emitting devices using the graphite nanofiber and preparing an anode electrode
10 with a light-emitting member such as a fluorescent substance.

The electron-emitting apparatus, light-emitting apparatus, and image display apparatus using the graphite nanofibers or carbon nanotubes can stably
15 emit electrons without keeping the interior in ultrahigh vacuum, unlike a conventional electron-emitting device. Since electrons are emitted with a low field, a high-reliability apparatus can be very easily manufactured. From
20 this, the manufacturing method of the present invention can be preferably applied to a device using the graphite nanofiber or carbon nanotube.

The fibrous carbon can be formed by decomposing hydrocarbon gas using a catalyst (material which
25 accelerate generating of carbon). The carbon nanotube and graphite nanofiber change depending on the type of catalyst and the decomposition

temperature.

As the catalyst material, Fe, Co, Pd, Ni, or an alloy of at least two materials selected from them is available as a nucleus (catalyst) for forming fibrous
5 carbon.

Particularly, Pd and Ni can generate a graphite nanofiber at low temperatures (temperature of 400°C or higher). Since the generation temperature of a carbon nanotube using Fe and Co must be 800°C or
10 higher, low-temperature formation of a graphite nanofiber material using Pd and Ni is preferable in terms of the influence on another member and the manufacturing cost.

The nucleus formation material can be palladium
15 oxide by using a property that an oxide is reduced by hydrogen at a low temperature (room temperature).

Hydrogen reduction processing for palladium oxide can form an initial aggregation nucleus at a relatively low temperature without using thermal
20 aggregation of a metal thin film or generation and vapor deposition of ultrafine particles conventionally used as a general nucleus formation method.

Examples of the hydrocarbon gas are hydrocarbon
25 gases such as acetylene, ethylene, methane, propane, and propylene, CO gas, CO₂ gas, and the vapor of an organic solvent such as ethanol or acetone.

When fibrous carbon is used for the electron-emitting member 4, the catalyst particle is applied to a desired region (on the cathode electrode 3), and introduced hydrocarbon gas is thermally decomposed. As a result, a bundle of a plurality of carbon fibers can be directly grown on the cathode electrode 3 via the catalyst particles. Alternatively, carbon fibers can be separately formed. In this case, carbon fibers are mixed in ink or paste and applied onto the cathode electrode 3 by printing or coating. The applied ink or paste is heated to form a bundle of carbon fibers on the cathode electrode 3. As printing or coating, various general printing methods can be applied. More specifically, a known method such as screen-printing, dispenser coating, and ink-jet printing can be adopted. In the example of Fig. 2, the cathode electrode 3 and conductive material 5 are separate members. However, the conductive material 5 is not always necessary, and may be made of the same material as that of the cathode electrode 3.

In order to suppress scattering of emitted electrons on the gate electrode in the electron-emitting device of the present invention, a plane which includes the surface of the electron-emitting member 4 and is substantially parallel to the surface of the substrate 1 is

preferably arranged at a position more apart from the substrate surface than a plane which includes part of the surface of the gate electrode 2 and is substantially parallel to the surface of the

5 substrate 1 (see Fig. 2). In other words, in the electron-emitting apparatus of the present invention, the plane which includes part of the surface of the electron-emitting member 4 and is substantially

10 parallel to the surface of the substrate 1 is arranged between the anode electrode 22 and the plane which includes part of the surface of the gate electrode 2 and is substantially parallel to the surface of the substrate 1 (see Fig. 2).

In the electron-emitting device of the present

15 invention, the electron-emitting member 4 is arranged at the height s (defined by the distance between the plane which includes part of the surface of the gate electrode 2 and is substantially parallel to the substrate 1 and the plane which includes the surface

20 of the electron-emitting member 4 and is substantially parallel to the surface of the substrate 1 (see Fig. 2)) at which no scattering substantially occurs on the gate electrode 2.

The height s depends on the ratio of a vertical

25 electric field intensity to a horizontal electric field intensity (vertical electric field intensity / horizontal electric field intensity). The height is

smaller as the ratio is higher, and larger as the ratio is lower. The practical range of the height s is 10 nm (inclusive) to 10 μm (inclusive).

The "horizontal electric field" in the present invention is "an electric field substantially parallel to the surface of the substrate 1", or "an electric field in a direction in which the gate electrode 2 and cathode electrode 3 face each other".

The "vertical electric field" in the present invention is "an electric field in a direction substantially perpendicular to the surface of the substrate 1", or "an electric field in a direction in which the substrate 1 and anode electrode 22 face each other".

In the electron-emitting apparatus of the present invention, as shown in Fig. 2, let d be the interval between the cathode electrode 3 and the gate electrode 2, V_f be the potential difference (voltage between the cathode electrode 3 and the gate electrode 2) upon driving the electron-emitting device, H be the distance between the anode electrode 22 and the surface of the substrate 1 on which the device is arranged, and V_b be the potential difference between the anode electrode 22 and the cathode electrode 3. In this case, the electric field intensity in driving (horizontal electric field intensity): $E_1 = V_f/d$ is set equal to or 50 times or

less than an anode-cathode electric field
intensity(vertical electric field intensity): $E_2 =$
 V_a/H .

This setting can reduce the ratio of electrons
5 which are emitted by the cathode electrode 3 and
collide against the gate electrode 2. Consequently,
a high-efficiency electron-emitting device with less
spread of an emitted electron beam can be obtained.

Driving of the electron-emitting device of the
10 present invention having electron-emitting members
with different electron-emitting threshold fields
will be explained with reference to Fig. 3. In
Fig. 3, the same reference numerals as in Fig. 2
denote the same parts.

15 In Fig. 3, the device is arranged in the vacuum
vessel 20, and a vacuum is produced using the
evacuation apparatus 25. A voltage is applied to the
device so as to apply a potential opposite to that in
Fig. 2, i.e., a high potential to the gate electrode
20 2 and a low potential to the electron-emitting member
4. At this time, the equipotential lines 23 are
shown in Fig. 3 are formed.

As is apparent from Fig. 3, an equipotential
line 23 having a specific potential is formed on the
25 surface of the electron-emitting member 4 such that
the equipotential line 23 comes close to the
electron-emitting member 4 in a region closest to the

gate electrode 2 and is spaced apart from the
electron-emitting member 4 as the line 23 is spaced
apart from the gate electrode 2. That is, on the
surface of the electron-emitting member 4, the
5 electric field intensity is high in a region close to
the gate electrode 2 and low in a region apart from
the gate electrode 2.

For this reason, electrons can be mainly
emitted from the area 24. That is, the step of
10 changing the above-mentioned electron-emitting
threshold field on the surface of the
electron-emitting member 4 is adopted while an
electric field intensity(strength) equal to or higher
than an electric field intensity(strength) necessary
15 for actual driving is applied. Electrons are mainly
emitted from the electron-emitting member 4 in a
region close to the gate electrode 2, and no
electrons are substantially emitted from an
electron-emitting member region apart from the gate
20 electrode 2.

This can prevent phenomena such as an abnormal
lights-on state in which electrons are emitted
without applying any potential to the gate electrode,
which poses a problem in the image forming apparatus.
25 [Examples]

Examples of the present invention will be
described in detail.

[Example 1]

Fig. 1A shows the state of an electron-emitting device fabricated in Example 1 when viewed from above the device. Fig. 1B is a sectional view taken along
5 the line 1B - 1B.

In Figs. 1A and 1B, the electron-emitting device is formed from an insulating substrate 1, extraction electrode 2, cathode electrode 3, electron-emitting member (emitter material) 4, and
10 conductive layer 5 on which fibrous carbon can grow.

The electron-emitting device manufacturing process of Example 1 will be explained in detail with reference to Figs. 4A to 4F.

(Step 1)

15 A quartz substrate was used as the substrate 1 and fully cleaned. After that, Ti and Pt were successively sputtered to thicknesses of 5 nm and 30 nm, respectively, as the gate electrode 2 and cathode (emitter) electrode 3.

20 A resist pattern was formed using a positive photoresist (AZ1500 available from Clariant) by photolithography.

The Pt and Ti layers were dry-etched by Ar gas using the patterned photoresist as a mask, thereby
25 forming an extraction electrode (gate electrode) 2 and cathode electrode 3 with an electrode gap d of 5 μm (Fig. 4A).

(Step 2)

The substrate temperature was kept at 300°C, TiN was deposited to a thickness of 500 nm by reactive sputtering of sputtering Ti with etching gas prepared
5 by mixing nitrogen in Ar, thereby forming a TiN layer 5' (Fig. 4B).

(Step 3)

After the substrate was sufficiently cooled to room temperature, Pd was deposited by an amount
10 enough to form an island by sputtering using Ar gas with the same evacuation apparatus as that in step 2, thus forming an island-like Pd layer 41 (Fig. 4C).

(Step 4)

A resist pattern was formed using a positive
15 photoresist (AZ1500 available from Clariant) by photolithography.

The island-like Pt layer 41 and TiN layer 5' were dry-etched by CF₄ gas using the patterned photoresist as a mask, thereby forming a metal
20 catalyst (island-like Pd layer 41) on only one electrode (i.e., cathode electrode 3) (Fig. 4D).

(Step 5)

Subsequently, the resultant structure was annealed at 500°C for 10 min in a flow of gas
25 prepared by mixing 1% hydrogen diluted with nitrogen at the atmospheric pressure and nitrogen-diluted 0.1% acetylene at 1 : 1. The structure was observed by a

scanning electron microscope to find that many fibrous carbon elements (electron-emitting members 4) about 5 nm to 250 nm in diameter which bent and fibrously extended were formed in the Pd formation region (Fig. 4D). At this time, the fibrous carbon thickness was about 5 μ m.

The device was set in a vacuum vessel 20 as shown in Fig. 2, and the interior of the vacuum vessel 20 was sufficiently evacuated to 2×10^{-5} Pa by an evacuation apparatus 25. Then, a valve for an H₂O etching gas 26 was opened to set a vacuum degree of 1×10^{-4} Pa in the vacuum vessel 20.

An anode voltage $V_a = 2$ kV was applied to an anode (anode electrode) 22 apart from the device by $H = 0.1$ mm. At that time, the cathode electrode 3 was set to ground potential, and a DC voltage ranging from $V_f = -10$ V to -100 V was applied to the gate electrode 2.

At the beginning of this step, electrons were emitted from a region of the electron-emitting member 4 apart from the gate electrode 2, and an electron current of about 50 μ A was observed. This current gradually decreased to 1 nA.

In this state, the device form was observed to find that fibers excessively longer than the average thickness of formed fibrous carbon decreased in the region of fibrous carbon (electron-emitting member 4)

apart from the gate electrode 2. Depending on the anode voltage V_a , distance H , and application voltage V_f , the average thickness of initial fibrous carbon tended to decrease as fibrous carbon was spaced apart
5 from the gate electrode 2 (see Fig. 4F).

The device was set in a vacuum vessel 20 as shown in Fig. 3, and the interior of the vacuum vessel 20 was sufficiently evacuated to 2×10^{-5} Pa by an evacuation apparatus 25.

10 Then, an anode voltage $V_a = 10$ kV was applied to the anode (anode electrode) 22 apart from the device by $H = 2$ mm. At that time, the cathode electrode 3 was set to ground potential, and a pulse voltage ranging from $V_f = +20$ V to $+100$ V was applied
15 to the gate electrode 2. For a device length (W in Fig. 1A) of $300 \mu\text{m}$, an electron-emitting current of $10 \mu\text{A}$ was observed.

Electrons were emitted by only the portion 24 shown in Fig. 3, and only one beam spot was confirmed
20 when the fluorescent substance was set on the anode side.

[Example 2]

Fig. 5 is a view showing an electron-emitting device in Example 2. In Fig. 5, the
25 electron-emitting device is formed from a substrate 1, lower electrode (gate electrode) 2, upper electrode (cathode electrode) 3, conductive layer 5

on which fibrous carbon can grow, electron-emitting member 4 made of a carbon material, anode substrate 51, anode electrode 52, and interlayer dielectric film 53. The manufacturing method of this device will be described below.

In Example 2, a soda lime-based high-strain-point glass substrate was used as the substrate 1.

A lower electrode 2 made of a silver-based wire about 3 μm in thickness and about 350 μm in width was formed on the substrate 1 using screen printing.

SiO_2 was sputtered as an interlayer dielectric film material to a thickness of about 1 μm on the entire substrate surface. Successively, Ti was sputtered to 5 nm (not shown due to a small thickness) as a layer contact to SiO_2 , and Pt was deposited as an upper electrode material to a thickness of about 100 nm.

Ti was sputtered to a thickness of 5 nm as the conductive layer 5 on which fibrous carbon can grow. Pd was sputtered into an island-like film 5 nm or less in thickness (not shown due to a small thickness) as a catalyst layer.

A pattern corresponding to the shape of the upper electrode 3 was formed using photolithography resist.

The substrate was set in a dry etching

apparatus. Pd as the catalyst layer and Ti as the fibrous carbon-growable conductive layer 5 were dry-etched away with SF_6 gas by using the resist pattern as a mask. Pt as the upper electrode material was dry-etched away using Ar gas, and Ti as the SiO_2 contact layer was removed using HBr gas.

SiO_2 as the interlayer dielectric film material was dry-etched away using a gas prepared by mixing proper amounts of CF_4 and H_2 . The resist used as a mask was removed to form an interlayer dielectric film 53 and upper electrode 3 having desired pattern shapes.

The substrate was set in a furnace, and gas in the furnace was satisfactorily exhausted. Thereafter, nitrogen-diluted 1% hydrogen and nitrogen-diluted 1% ethylene were introduced into the furnace up to the atmospheric pressure at a ratio of 1 : 1.

After the substrate was heated to 600°C and kept for 30 min. in the furnace, black fibrous carbon (electron-emitting member) 4 was grown on the entire upper electrode.

The grown fibrous carbon was observed by a transmission electron microscope to find that graphene was formed in a multilayered structure, as shown on the right side of Fig. 9.

The step of changing the electron-emitting

threshold field of the electron-emitting member was the same as that in Example 1.

In Example 2, a pulse voltage was used to apply a low potential to the gate electrode 2. When pulses stop, the electron-emitting threshold field of a region of the electron-emitting member 4 apart from the gate electrode 2 changes. In addition, the electron-emitting threshold field of a region of the electron-emitting member 4 close to the gate electrode 2 increases. Hence, with the use of the pulse method, like Example 2, the electron-emitting threshold field between devices could be set to a desired value. The increase ratio over time could be controlled by changing the pulse duty.

[Example 3]

Example 3 concerns an image forming apparatus constituted using an electron source obtained by arranging a plurality of electron-emitting devices of the present invention. The electron source will be described with reference to Fig. 6.

In Fig. 6, the electron source is made up of an electron source substrate 61, X-direction wiring lines 62, Y-direction wiring lines 63, electron-emitting devices 64 of the present invention, and connections 65.

If the device capacitance increases owing to the arrangement of a plurality of electron-emitting

devices, the waveforms becomes blunt due to the capacitive component even upon application of a short pulse accompanying pulse width modulation, failing to obtain an expected tone level. In Example 3, an
5 interlayer dielectric film was arranged to reduce an increase in capacitive component at a portion other than the electron-emitting portion.

In Fig. 6, m X-direction wiring lines 62 include $Dx1, Dx2, \dots, Dxm$, and are made of an
10 aluminum-based wiring material about $1 \mu m$ in thickness and $300 \mu m$ in width formed by vapor deposition. The wiring material, film thickness, and width are appropriately designed. The Y-direction wiring lines 63 include n wiring lines $Dy1, Dy2, \dots$,
15 Dyn $0.5 \mu m$ in thickness and $100 \mu m$ in width, and are formed similarly to the X-direction wiring lines 62. An interlayer dielectric film (not shown) is interposed between the m X-direction wiring lines 62 and the n Y-direction wiring lines 63, and
20 electrically insulates them. The X- and Y-direction wiring lines 62 and 63 are extracted as external terminals. Note that m and n represent positive integers.

The interlayer dielectric film (not shown) was
25 formed from SiO_2 about $5 \mu m$ in thickness by sputtering or the like. All or part of the surface of the substrate 61 on which the X-direction wiring

lines 62 were formed was formed into a desired shape.
To resist the potential difference at the
intersection between the X- and Y-direction wiring
lines 62 and 63, the thickness of the interlayer
5 dielectric film was so determined as to attain a
device capacitance of 1 pF or less per device and a
device breakdown voltage of 30 V.

gate electrode and cathode electrode Pairs (not
shown) which constitute the electron-emitting devices
10 64 of the present invention are electrically
connected by the m X-direction wiring lines 62, the n
Y-direction wiring lines 63, and the connections 65
made of a conductive metal or the like.

Each X-direction wiring line 62 is connected to
15 a scanning signal application means (not shown) for
applying a scanning signal for selecting a row of
electron-emitting devices 64 of the present invention
aligned in the X direction. Each Y-direction wiring
line 63 is connected to a modulation signal
20 generation means (not shown) for modulating in
accordance with an input signal each array of the
electron-emitting devices 64 of the present invention
aligned in the Y direction. A driving voltage
applied to each electron-emitting device is supplied
25 as a difference voltage between the scanning and
modulation signals supplied to the device.

If X-direction rows and Y-direction arrays

increase in a matrix as shown in Fig. 6, the application voltage to respective devices may vary due to the voltage drop in selecting all the electron-emitting devices in the matrix and
5 performing the threshold field control step at once. To prevent this, the threshold field control step is preferably executed line-sequentially or point-sequentially.

The line-sequential threshold field control
10 step will be described. For example, the same voltage is applied to the n Y-direction wiring lines $Dy1, Dy2, \dots, Dyn$. A positive voltage with respect to the Y-direction wiring line is applied to $Dx1$ to select electron-emitting devices on the row $Dx1$ and
15 perform threshold field control processing. Then, the same voltage is applied to $Dx2$ to select electron-emitting devices on the row $Dx2$ and perform threshold field control processing. Similarly, the rows $Dx3, Dx4, \dots, Dxm$ are selected to sequentially
20 perform threshold field control processing in the X direction. This processing can reduce the influence of the voltage drop.

The point-sequential threshold field control step is a method of selecting individual devices so
25 as to enable independently driving them by using the matrix wiring, and performing the threshold field control step sequentially for the electron-emitting

devices one by one. This method is free from the influence of the voltage drop, but the processing time is proportional to the number of devices. Thus, line-sequential processing, point-sequential

5 processing, and simultaneous processing are chosen in accordance with the size of the electron source and the use purpose.

In Example 3, an anode whose entire substrate surface was covered with an ITO film (Indium Tin
10 Oxide compound) was set at a height $H = 0.3$ mm above the matrix substrate, and the anode voltage V_a was set to 6 kV.

Then, O_2 was introduced into the vacuum vessel so as to set the interior to 1×10^{-4} Pa. The n
15 Y-direction wiring lines Dy_1, Dy_2, \dots, Dy_n were commonly grounded. The pulse voltage $V_f = -50V$ to $-100 V$ (pulse voltage width: 1 msec, pulse interval: 10 msec) was applied to Dx_1 to select electron-emitting devices on the row Dx_1 and perform
20 threshold field control processing. The same voltage was applied to Dx_2 to select electron-emitting devices on the row Dx_2 and perform threshold field control processing. Similarly, the rows Dx_3, Dx_4, \dots, Dx_m were selected and sequentially underwent
25 threshold field control processing in the X direction.

As a result, the same threshold field control

as that of a single-bit device could be achieved on all the devices.

As has been described above, the electron-emitting device and electron source
5 according to the present invention can emit electrons from only a region of the electron-emitting member close to the extraction electrode.

The image forming apparatus constituted using the electron source of the present invention can form
10 a high-quality image almost free from brightness nonuniformity and abnormal lights-on errors. A high-quality image forming apparatus such as a flat high-definition color television can be implemented.

WHAT IS CLAIMED IS:

1. An electron-emitting device comprising:
an electron-emitting member containing carbon as a
main component; and
5 an extraction electrode arranged near the
electron-emitting member, wherein an
electron-emitting threshold field of the
electron-emitting member is low at a portion close to
the extraction electrode and high at a portion apart
10 from the extraction electrode.
2. An electron-emitting device according to
claim 1, wherein the electron-emitting member
containing carbon as a main component includes a
15 plurality of fibrous carbon elements, and the fibrous
carbon elements are made of a material which has an
 sp^2 bond and is selected from the group consisting of
a graphite nanofiber, a carbon nanotube, amorphous
carbon, and a mixture of at least two materials
20 selected from the group consisting of the graphite
nanofiber, the carbon nanotube, and amorphous carbon.
3. An electron-emitting device according to
claim 1, wherein the electron-emitting member
25 containing carbon as a main component includes a thin
film made of a material which has an sp^3 bond and is
selected from the group consisting of diamond,

diamond-like carbon, amorphous carbon, and a mixture of at least two materials selected from the group consisting of diamond, diamond-like carbon, and amorphous carbon.

5

4. An electron source comprising at least one electron-emitting device array constituted by arranging a plurality of electron-emitting devices defined in claim 1 parallel to each other and
10 connecting the electron-emitting devices.

5. An electron source comprising at least one electron-emitting device array constituted by arranging a plurality of electron-emitting devices
15 defined claim 1,

wherein low-potential supply wiring lines and high-potential supply wiring lines, which drive the electron-emitting devices are arranged in a matrix.

20 6. An image forming apparatus comprising said electron source defined in claim 4 or 5, and an image forming member which forms an image by electrons emitted by said electron source,

wherein an electron-emitting amount of each
25 electron-emitting device of said electron source is controlled by an information signal.

7. A method of manufacturing an
electron-emitting device having an electron-emitting
member containing carbon as a main component, and an
extraction electrode arranged near the
5 electron-emitting member, the method comprising:
a threshold field control step of performing
processing so as to give an electron-emitting
threshold field of the electron-emitting member a
different value depending on a distance from the
10 extraction electrode.

8. A method according to claim 7, wherein the
electron-emitting member containing carbon as a main
component includes a plurality of fibrous carbon
15 elements, and the fibrous carbon elements are made of
a material which has an sp^2 bond and is selected from
the group consisting of a graphite nanofiber, a
carbon nanotube, amorphous carbon, and a mixture of
at least two materials selected from the group
20 consisting of the graphite nanofiber, the carbon
nanotube, and amorphous carbon.

9. A method according to claim 7, wherein the
electron-emitting member containing carbon as a main
25 component includes a plurality of fibrous carbon
elements, and the fibrous carbon elements include a
thin film made of a material which has an sp^3 bond

and is selected from the group consisting of diamond,
diamond-like carbon, amorphous carbon, and a mixture
of at least two materials selected from the group
consisting of diamond, diamond-like carbon, and
5 amorphous carbon.

10. A method according to claim 7, wherein the
threshold field control step includes a step of
partially etching the electron-emitting member in an
10 atmosphere of a substance which can chemically react
with the electron-emitting member.

11. A method according to claim 10, wherein the
substance which can chemically react with the
15 electron-emitting member includes water, oxygen, and
carbon dioxide.

12. A method according to 7, wherein in the
threshold field control step, the electron-emitting
20 member emits electrons.

13. A method according to 7, wherein in the
threshold field control step, a negative potential
with respect to the electron-emitting member is
25 applied to the extraction electrode, and a positive
potential with respect to the electron-emitting
member is applied to an anode arranged in opposite to

the electron-emitting member via vacuum.

14. A method of manufacturing an electron source
in which at least one array of a plurality of
5 electron-emitting devices is arranged on an
insulating substrate, and low-potential supply wiring
lines and high-potential supply wiring lines which
drive the electron-emitting devices are arranged in a
matrix, the method comprising:
10 manufacturing the electron-emitting devices by
the manufacturing method defined in claim 7.

15. A method according to claim 14, wherein the
threshold field control step is line-sequentially
15 performed by selecting an array of the
electron-emitting devices and driving each array.

16. A method according to claim 15, wherein the
threshold field control step is point-sequentially
20 performed by selecting an electron-emitting device
and driving the selected device.

ABSTRACT OF THE DISCLOSURE

In an electron-emitting device having an electron-emitting member containing carbon as a main component, and an extraction electrode arranged near
5 the electron-emitting member, electrons can be emitted by substantially only a region of the electron-emitting member close to the extraction electrode. Brightness nonuniformity and abnormal lights-on errors are reduced in an image forming
10 apparatus in which the electron-emitting devices are constituted into an electron. The electron-emitting threshold field of the electron-emitting member is set low at a portion close to the extraction
15 extraction electrode and high at a portion apart from the extraction electrode.

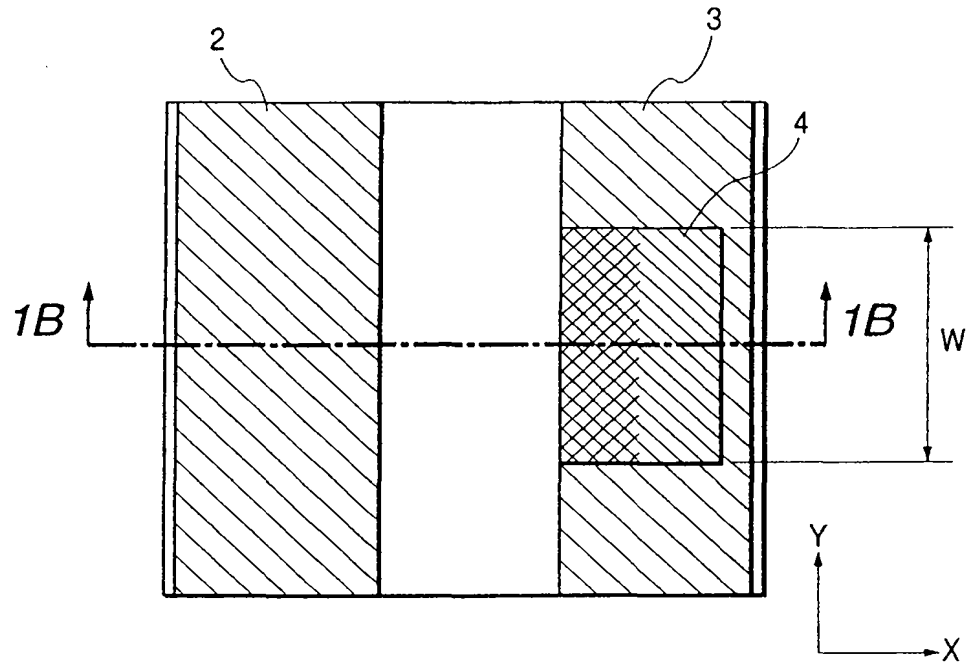
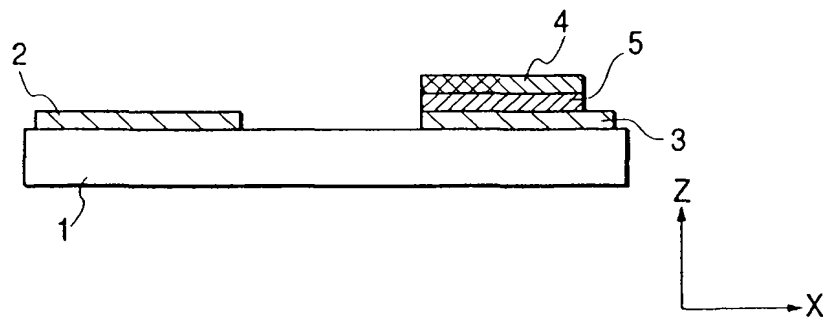
FIG. 1A*FIG. 1B*

FIG. 2

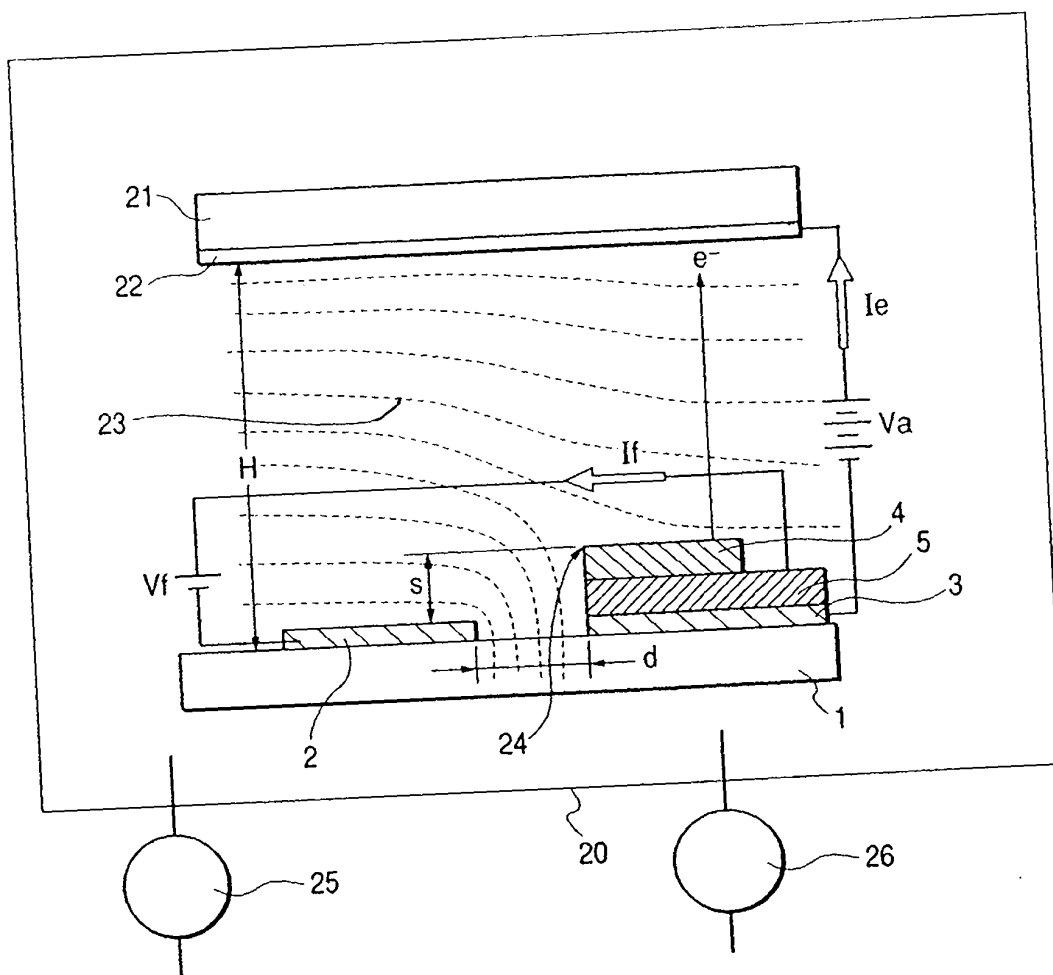


FIG. 3

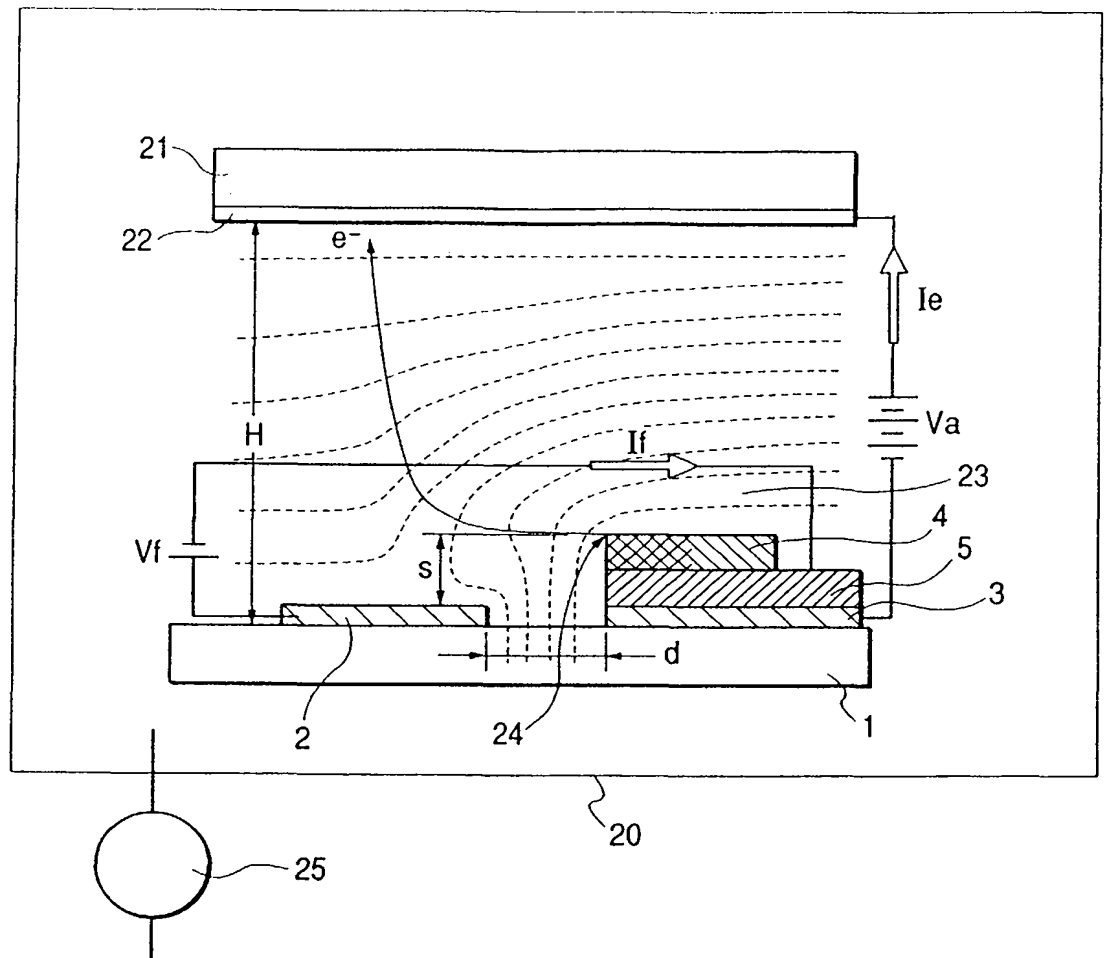


FIG. 4A

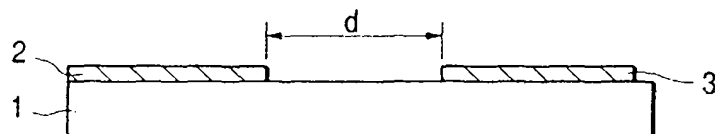


FIG. 4B

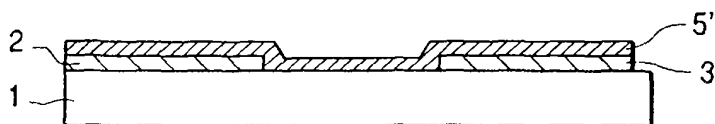


FIG. 4C

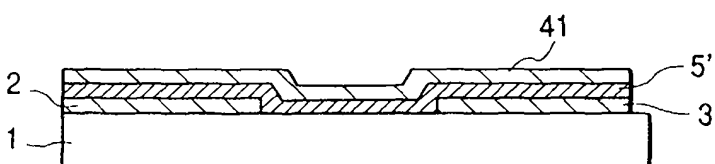


FIG. 4D

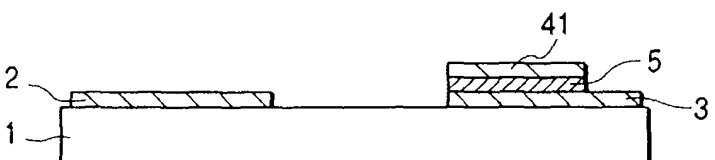


FIG. 4E

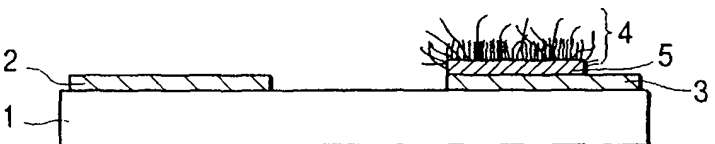


FIG. 4F

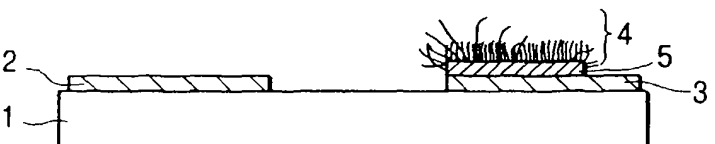


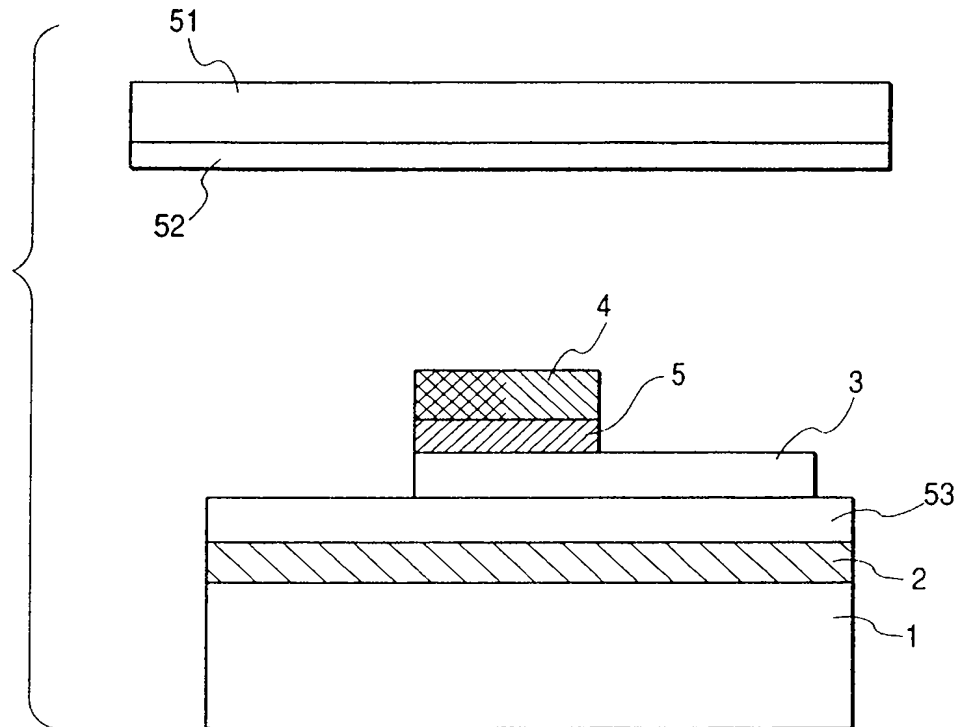
FIG. 5

FIG. 6

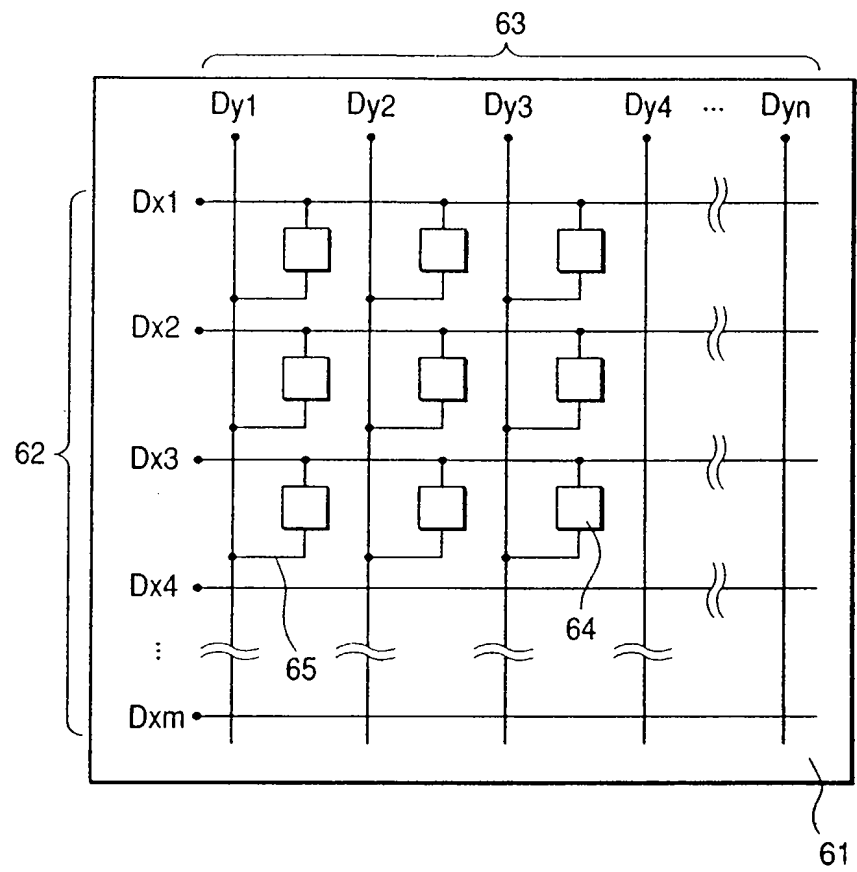


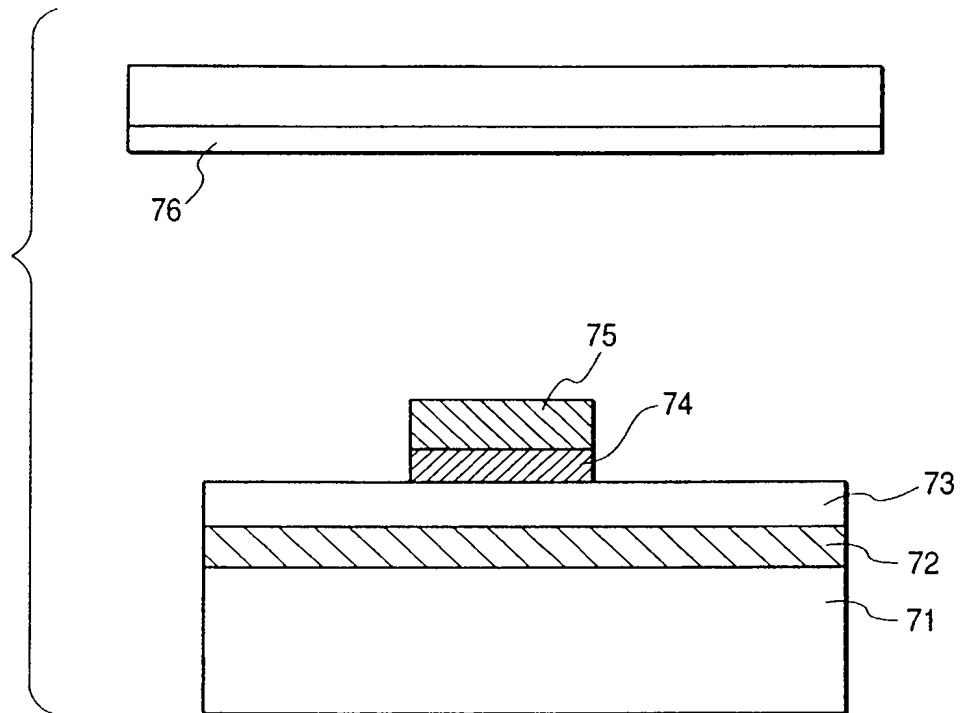
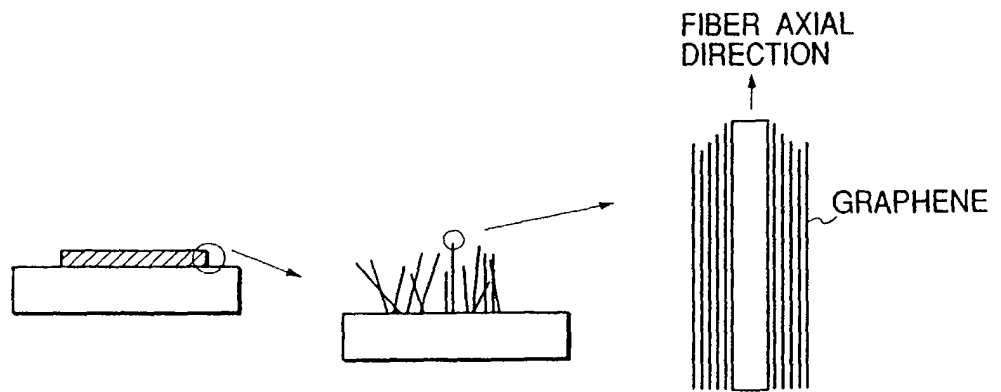
FIG. 7

FIG. 8*FIG. 9*